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SUMMARY

The effect of cupric chloride on the free radical polymerisation of acrylonitrile and of several copper salts on the free radical polymerisation of methyl methacrylate has been examined.

Cupric chloride in dimethyl formamide was found to inhibit the homogeneous polymerisation of acrylonitrile initiated by α,α'-azo-bis-isobutynonitrile at 60°C. The rate of polymerisation following the inhibition period was invariably less than the rate obtained in the absence of cupric chloride, and varied inversely with initial cupric chloride concentration for high initial cupric chloride concentrations. The corrected value of the rate constant for the initiation reaction obtained from plots of inhibition period against initial cupric chloride concentration was $1{\cdot}51 \times 10^{-5}$ sec^{-1}. A corrected value of 5·7 for k_y/k_p was obtained from the plot of final retarded rate of polymerisation against the reciprocal of the initial cupric chloride concentration, where k_y is the rate constant for the reaction between growing polyacrylonitrile radicals and the inhibition product. The ratio k_x/k_p was determined from rate measurements during the period of acceleration following complete inhibition and found to have a mean value of 100 at 60°C. Using a value of 1930 l.mole^{-1}sec^{-1} for k_p at 60°C, values of $1{\cdot}93 \times 10^5$ and $1{\cdot}1 \times 10^4$ l.mole^{-1}sec^{-1} are obtained for k_x and k_y respectively.

In the polymerisation of methyl methacrylate initiated by α,α'-azo-bis-isobutyronitrile, cupric chloride and cupric bromide inhibit the polymerisation whereas cupric acetate and cupric

nitrate have no effect on the rate of polymerisation. In all cases dimethyl formamide was used to combat the insolubility of the copper salts in methyl methacrylate. With the cupric halides the post-inhibition rate is equal to the rate obtained in the absence of inhibitor. From the plots of inhibition period against copper salt concentration rate constants of initiation of $1{\cdot}38 \times 10^{-5} sec^{-1}$ and $1{\cdot}40 \times 10^{-5} sec^{-1}$ were obtained using cupric chloride and cupric bromide respectively as inhibitor. From a study of the period of acceleration following complete inhibition values were obtained for the ratio k_x/k_p where k_x is the rate constant for the reaction between polymethyl methacrylate radicals and cupric salt. k_x/k_p values of 1050 and 2190 were obtained for the cupric chloride and cupric bromide reactions respectively. Using a value of 734 $l.mole^{-1}sec^{-1}$ for k_p at 60°C, values of $7{\cdot}7 \times 10^5$ and $1{\cdot}6 \times 10^6$ $l.mole^{-1}sec^{-1}$ are obtained for k_x for the cupric chloride and cupric bromide reactions. Addition of small quantities of water to the cupric chloride inhibited polymerisation of methyl methacrylate resulted in an increase in the rate of initiation and a decrease in the k_x/k_p ratio.

The cupric chloride and cupric bromide inhibited polymerisation of methyl methacrylate initiated by α,α'-azo-bis-isobutyronitrile was examined at a range of temperatures between 40°C and 72°C. From a plot of log $2k_i$ against $1/T°K$ a value of 32·9 kcal/mole was obtained for the energy of activation for initiation. The overall activation energy for the polymerisation was determined by plotting $\log_{10}\{\text{rate}/[\text{initiator}]^{0{\cdot}5}\}$ against $1/T°K$ and was found to be 20·5 kcal/mole. The lack of reproducibility in the k_x/k_p values at the different temperatures

prevented an accurate determination of the corresponding activation energies.

The rate of removal of cupric chloride in the different monomer/solvent systems in the presence of α,α' -azo-bis-isobutyronitrile at 60°C were measured spectrophotometrically. The results, in general, showed poor agreement with the dilatometric studies, and indicated different complex formations in the different solvent systems.

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INTRODUCTION

Bamford et al.[1-4] have studied the effects of ferric chloride in non-aqueous media on the free radical polymerisation of some vinyl monomers. With vinyl acetate and styrene the polymerisation was inhibited, while with methyl acrylate, methyl methacrylate, acrylonitrile and methacrylonitrile retardation occurred. In both cases when ferric chloride was used it was reduced to ferrous chloride according to the equation:

$$\sim\!CH_2 - \dot{C}HX + FeCl_3 \longrightarrow FeCl_2 + \begin{matrix} \sim\!CH_2 - CHXCl \text{ or} \\ \sim\!CH = CHX + HCl. \end{matrix}$$

The rate of formation of ferrous chloride has been shown to give a measure of the rate of initiation of the polymerisation. The authors have carried out a detailed kinetic study of the polymerisation and proposed a kinetic scheme whereby the rate constants for the termination reaction can be evaluated. The results show that the order of reactivity of the polymer radicals to ferric chloride is inconsistent with the general reactivity of the radicals.

With the possibility of other metal salts reacting in a similar manner to ferric chloride, a study has been made on the effects of some copper salts on the polymerisation of methyl methacrylate and acrylonitrile. During the course of this work

we became aware of work by Monteiro and Parrod [5,6] on the effects of cupric chloride on the polymerisation of styrene and acrylonitrile in dimethylformamide solution. They found that cupric chloride inhibits both polymerisations, but with styrene the inhibition period is followed by a rapid acceleration to the normal rate in the absence of an inhibitor, whereas with acrylonitrile, it is followed by a retarded rate, the degree of retardation being greater, the greater the initial concentration of cupric chloride. The results obtained for acrylonitrile agree in general with those of Monteiro and Parrod.

The main work in this thesis concerns the effects of various copper salts on the polymerisation of methyl methacrylate. Cupric chloride and bromide both inhibit the polymerisation, the inhibition period being rapidly followed by the normal uninhibited rate of polymerisation, while cupric acetate and cupric nitrate have no effect on the rate of polymerisation at 60°C initiated by 1,1'-azo-bis-isobutyronitrile. The cupric halides are thus suitable inhibitors for measuring rates of initiation in this system, and the results obtained in this study are in good agreement with those obtained by Bamford et al. using ferric chloride [4]. An attempt has been made to correlate these results with the rate of removal of cupric chloride from a similar system, measured spectrophotometrically.

To obtain more information regarding the reactivity of polymer radicals with metal salts, the rate constants for the reactions between polymethyl methacrylate radical with cupric chloride and bromide have been evaluated by means of a kinetic scheme, modified from that of Bamford et al., and also by an

alternative scheme which has been proposed. It was found that the value of the rate constant for cupric bromide is approximately twice that for cupric chloride, and approximately 4×10^2 times that for the equivalent reaction of ferric chloride. Small quantities of water in the system were found to cause a reduction in the value of k_x/k_p, the ratio of the rate constants of termination by cupric salts and propagation respectively.

In order to understand the significance of this work more fully, a survey of previous work on the interaction of polymer radicals with metal salts has been made.

PREVIOUS WORK ON THE INTERACTION OF POLYMER RADICALS WITH METAL SALTS.

In recent years it has been clear that the cations of variable valence can be oxidised or reduced by organic radicals [7,8].

The studies in this field may be roughly divided into two sections, namely, reactions in aqueous and non-aqueous solution respectively. As the latter is the more recent study and more closely related to this present work, it will be considered after a survey of the work in aqueous solution.

Evans et al.[9,10] showed that U.V. irradiation of aqueous solutions of ferric perchlorate in acid solution produced free radicals. The mechanism was considered to involve electron transfer within the active species ($Fe^{3+}OH^-$), as follows:

$$Fe^{3+}OH^- \xrightarrow{h\nu} Fe^{2+}OH \longrightarrow Fe^{2+} + OH^{\bullet} .$$

They showed that the radicals produced could initiate the polymerisation of acrylonitrile.

In a similar system, Dainton and Tordoff [11] found, in the polymerisations of acrylonitrile and to a lesser extent of methyl methacrylate, many metal ions are effective terminating agents:

$$R_n^{\bullet} + Fe^{3+}aq. \longrightarrow P_nOH + H^+ + Fe^{2+}$$

$$R_n^{\bullet} + Fe^{3+}OH^- \longrightarrow P_nOH + Fe^{2+} \quad .$$

This was supported by the results of Bates and Uri [12] on the oxidation of aromatic compounds in aqueous solution in which they concluded that organic radicals can reduce ferric ion complexes.

An extensive study of the termination of vinyl polymerisation by metal ions in aqueous solution has been carried out by Dainton et al., using various modes of initiation [13-21]. With ferric chloride, it has been shown, in certain circumstances, that the rate of formation of divalent iron can be identified with the rate of initiation of polymerisation. Recently, the effects of a series of metal salts on the polymerisation of acrylamide initiated by ionizing radiation have been studied. Using steady state kinetics they have measured the rate constants for the termination reaction between polyacrylamide radicals and metal salts, and have shown that neither the rate constants, nor entropies, nor energies of activation of these reactions can be correlated with thermodynamic properties of the redox system. It is postulated that entirely non thermodynamic influences dominate these reactions. The authors suggest that the oxidation of the radical involves the utilization of one of the vacant d-orbitals of the cation, and envisage the approach of the radical to the cation so as to achieve sufficient overlap of the p-orbital of the carbon and a d-orbital of the cation in the

transition state for rapid electron transfer to take place. The release of an electron by the radical enables it to expel a proton. On this hypothesis the overall reaction might be represented in the case of the cupric ion:

$$Cu^{2+}_{3d^9} + {}^{\bullet}CH(x)CH_2m_{j-1} \longrightarrow \underset{\text{transition state}}{(Cu\cdots CH(x)\text{-}\underset{H}{CH}\text{-}m_j)^{2+}} \longrightarrow Cu^{+}_{3d^{10}} + CH(x)=CHm_{j-1} + H^{+}$$

(where x = $CONH_2$)

The mechanism of electron flow via a bridged activated complex was postulated by Taube and Meyers [22] in the oxidation of chromous ion by chloro pentamino cobalt ion.

$$\left[Co(NH_3)_5Cl\right]^{2+} + Cr^{2+} \longrightarrow \left[Co(NH_3)_5\right]^{2+} + CrCl^{2+}$$

Quantitative transfer of a chlorine atom to the reducing agent takes place with no exchange with chlorine ions in solution. Thus it is maintained that reaction takes place only through the formation of a chlorine bridged transition state.

Watanabe and Kiuchi [23] have recently examined the effects of cupric salts on the polymerisation of acrylonitrile in aqueous solution initiated by ammonium persulphate. They found that the presence of cupric sulphate, nitrate or acetate caused an increase in the rate of polymerisation of acrylonitrile, but no increase in rate was found in the polymerisation of other monomers such as methyl acrylate, vinyl acetate, methyl methacrylate and acrylamide. The increased rate is attributed to the following reactions:

$$CH_2 = CHCN + Cu^{++} \longrightarrow CH_2 = \dot{C}CN + Cu^{+} + H^{+}$$

$$Cu^{+} + S_2O_8^{=} \longrightarrow SO_4^{\bullet -} + SO_4^{=} + Cu^{++}.$$

Both cupric chloride and bromide retarded or completely inhibited the polymerisation beyond certain salt concentrations and the authors suggest that the complex ion CuX^{+}(X=Cl,Br) is a more efficient terminator for polymer chains than Cu^{++}aq.. The termination reaction is represented by the reactions:

$$\sim CH_2\dot{C}HCN + CuX^{+} \longrightarrow \sim CH_2\underset{X}{\underset{|}{C}}HCN + Cu^{+}$$

$$\sim CH_2\dot{C}HCN + CuX_2 \longrightarrow \sim CH_2\underset{X}{\underset{|}{C}}HCN + CuX \quad .$$

Dainton et al. [17-20] have examined the aqueous acrylonitrile system. They found that in this system there are two chain carriers, a water soluble short chain polyacrylonitrile radical which propagates rapidly and is susceptible to rapid mutual termination and to oxidation by ferric ions, and a water suspended particle containing a polyradical which propagates slowly by interaction with another particle or a water-soluble radical. The radicals embedded in particles are only oxidised by metal salts if they can be penetrated by them, and this penetration normally does not occur until the uncharged species are present in significant amounts [24]. Thus Dainton suggests that for examination of the reaction between metal salts and polymer radicals from measurements of rate and degree of polymerisation, it is essential to use a soluble radical such as polyacrylamide, which undergoes propagation and mutual termination at the same rate over a wide pH range. This enables absolute rate constants in aqueous solution to be determined for the reaction of a given polyradical with a metal ion. For such a system, Dainton et al. have found the rate constant for the oxidation of polyacrylamide radicals by Fe^{3+} and Cu^{2+} ions to be $2{\cdot}7 \times 10^{3}$ l.mole^{-1}sec.$^{-1}$ and

$1{\cdot}2 \times 10^{3}$ l.mole^{-1}sec.$^{-1}$ respectively. More recently, Dainton and Sisley [25] have examined the termination reaction between ferric ions and polymethacrylamide radicals in aqueous solution and have shown that a ferric ion - methacrylamide complex plays a significant part in the reaction.

Bamford et al.[1-4] extended the study to systems in non-aqueous media, thus eliminating the restriction imposed on previous work by the insolubility of most vinyl monomers in H_2O. They have studied the effects of ferric chloride in dimethyl formamide solution on the polymerisation of various vinyl monomers and, as stated earlier, showed that ferric chloride terminated the polymer chains; the ferric chloride in all cases being reduced to ferrous chloride in the termination reaction. The rate of formation of ferrous chloride gave a measure of the rate of initiation of the polymerisation while detailed kinetic studies led to the evaluation of the rate constants of the reaction between ferric chloride and the polymer radicals. A similar approach by Betts, Dainton and Ivin [26] has been used to determine the kinetics of decomposition of 1,1'-azo-bis-isobutyronitrile in dimethylformamide solution.

Bamford et al. show that for the polymerisation initiated by AIBN at 60°C, the rate of initiation is independent of the nature of the monomer [4]. For the monomers studied they found the order of reactivity of the polyradicals to ferric chloride as:

vinyl acetate > styrene > methyl acrylate > acrylonitrile > methyl methacrylate > methacrylonitrile.

Thus it became clear that the reaction rate is not completely determined by the general reactivity of the radical concerned. Bamford et al. [27] have carried out an extensive study on the polar

properties of the substituents carried by the radicals with respect to the general reactivities. This is proposed as a major factor in the mechanism and the transition state in the radical-ion reaction may be visualised as involving the partial transference of an electron from the radical to the ferric ion. Otherwise, the transition state contains contributions from the structures

$$R^{\cdot}Fe^{3+} \longleftrightarrow R^{+}Fe^{2+} \quad .$$

Thus radicals carrying electron-attracting substituents will react less readily than would be expected from their general reactivity.

Electron transfer, therefore, is a major factor in the radical-ion reaction. Entwhistle [28], however, introduced another factor in the mechanism. The reactivities of a series of ferric salts to polymethyl methacrylate radicals were examined, and it was found that these varied greatly. The order of reactivity is

bromide > chloride > benzoate > perchlorate.

Entwhistle observes that this is also the order of decreasing tendency to hydrolyse and concludes that the bond strength of the ferric salt is an important factor in determining its reactivity to polymer radicals. These reactions suggest that the overall reaction is one of electron transfer through some form of transition state, possibly a bridged activated complex of the type proposed by Taube and Meyers.

Kumamoto et al.[29] used cupric and ferric chloride in trapping radical intermediates and their results favour a chlorine bridged transition state in which chlorine is transferred to an alkyl radical by an oxidising metal ion:

$$R^{\bullet} + M^{n}Cl_{n} \longrightarrow \left[R^{\bullet}\ldots Cl\ldots M^{n}Cl_{n-1}\right] \longrightarrow RCl + M^{n-1}Cl_{n-1} \quad .$$

Kochi [30] has examined the reactions resulting from the photolysis of cupric chloride in organic solvents. They are described as the addition and abstraction reactions of chlorine. They postulate that the photolysis occurs by initial fission to form cuprous chloride and chlorine atoms. Chlorine atom reactions are proposed as the second step and chain termination as involving the reaction of cupric chloride with carbon radical intermediates. The reactions may be formulated in the case of isopropyl alcohol as follows:

$$CuCl_2 \underset{}{\overset{h\nu}{\rightleftharpoons}} CuCl + Cl^{\bullet}$$

$$(CH_3)_2CHOH + Cl^{\bullet} \longrightarrow (CH_3)_2\dot{C}OH + HCl$$

$$(CH_3)_2COH + CuCl_2 \longrightarrow \left[(CH_3)_2C(OH)Cl\right] + CuCl$$

$$\left[(CH_3)_2C(OH)Cl\right] \longrightarrow CH_3COCH_3 + HCl \quad .$$

Monteiro and Parrod [5] studied the effect of various metal chlorides on the polymerisation of acrylonitrile in dimethylformamide solution. The effects of the chlorides fall into three catagories:

1. Accelerators - $LiCl$, $MgCl_2$, $BeCl_2$, $AlCl_3$;
2. Retarders - $CuCl_2$, $FeCl_3$;
3. No effect - $CoCl_2$, $NiCl_2$, $CrCl_3$.

More recently Monteiro [6] has examined the inhibition of acrylonitrile and styrene by cupric chloride as stated earlier.

By studying the reactions of copper salts in the polymerisation of methyl methacrylate it was hoped that some additional information regarding these systems will be obtained. This may eventually lead to the complete understanding of the reactions between metal salts and polymer radicals.

INITIATION, INHIBITION, RETARDATION AND POLYMERISATION KINETICS.

Rates of initiation can be determined in two ways.

(1) Calculation from other measured quantities of the system.

Considering the simple kinetic scheme for vinyl polymerisation as:

		Rate	
Initiation	$\longrightarrow R_1^{\bullet}$	I	(1.i)
Propagation	$R_n^{\bullet} + M \longrightarrow R_{n+1}^{\bullet}$	$k_p[R_n^{\bullet}][M]$	(1.ii)
Chain Transfer	$R_n^{\bullet} + M \longrightarrow P_n + R^{\bullet}$	$k_{tr}[R_n^{\bullet}][M]$	(1.iii)
Termination	$R_n^{\bullet} + R_m^{\bullet} \longrightarrow$ Polymer	$k_t[R_n^{\bullet}]^2$	(1.iv)

Where M represents a monomer molecule, P_n an inactive polymer molecule comprising n monomer units and $R_n^{\bullet}$ a polymer radical comprising n monomer units. I is the rate of initiation; k_p, k_{tr} and k_t are the rate constants of propagation, chain transfer and termination respectively.

Assuming stationary state conditions, with $[R]_s \equiv$ the stationary radical concentration, and the reactivity of the radicals independent of n, then it can be shown that

$$-\frac{d[M]}{dt} = \frac{k_p I^{\frac{1}{2}}[M]}{k_t^{\frac{1}{2}}} \qquad (2)$$

If the degree of polymerisation, $\bar{DP}$, is defined as the average number of monomer units consumed per polymer chain terminated, then

$$\bar{DP} = \frac{k_p[R]_s[M]}{k_t[R]_s^2 + k_{tr}[R]_s[M]} \qquad (3)$$

$$\therefore \quad \frac{1}{\bar{DP}} = \frac{k_{tr}}{k_p} - \frac{k_t}{k_p^2[M]^2}\frac{d[M]}{dt} \qquad (4)$$

From this relation (4), k_t/k_p^2 can be obtained by plotting $1/\bar{DP}$ against $-d[M]/dt$. A necessary condition being that k_{tr}/k_p should not be too great, otherwise the determination becomes very insensitive. Thus from the two composite constants in equation (2) and (4), I, the rate of initiation may be obtained. In this treatment, however, a single termination reaction has been assumed; and unless the precise mode of termination is known, whether by disproportionation or by combination, or if both processes occur, the relative extent of each, the calculated rates of initiation by this method is subject to an uncertainty factor of 2 from this cause alone. Additional errors in the value of $\bar{DP}$ may arise from the loss of the more soluble low molecular weight fractions of polymer during precipitation, and in osmotic pressure measurements by diffusion of low molecular weight polymer through the membrane.

Bamford and Dewar [31] used a method, similar in principle to the one just described, for measuring rate constants in vinyl polymerisation including the rate of initiation. The method depends

essentially on the measurement of the rate of increase of viscosity during polymerisation for various rates of chain initiation.

Also, since the mean kinetic chain length, v, i.e. the average number of monomer molecules consumed per chain started, is given by

$$v = -\frac{1}{I}\frac{d[M]}{dt}, \qquad (5)$$

then I may be obtained from a knowledge of v and the rate of polymerisation. The value of v is obtained by using an initiator giving fragments which can be determined in the polymer, providing the analytical method used has the required degree of precision. For example, Bevington et al.[32] measured v by using a radioactive catalyst, C^{14}- labelled azo-bis-isobutyronitrile, and estimating the amount of initiator fragments in the polymer from radioactivity measurements on CO_2 produced by combustion of the polymer. The ratio of monomer units to initiator fragments in the polymer is clearly equal to v if each initiator radical starting a chain is incorporated into the polymer, regardless of whether termination is by combination or disproportionation. It is therefore necessary to assume that all the initiating radicals react with the monomer by addition to double bonds rather than by hydrogen abstraction, and this is justified from energy considerations. There should be no transfer with initiator molecules or termination with initiator radicals and initiation by processes other than catalyst decomposition must be negligible; these can readily be checked experimentally. In this method also, it is essential to ensure that no low molecular weight polymer is lost in the isolation of the reaction product and uncombined initiator must be removed from the polymer.

(11) The estimation of the rate of production of free radicals by use of a scavenger.

The rate of polymerisation of a vinyl monomer may be reduced or almost completely supressed by the addition of relatively small quantities of certain substances, sometimes referred to as scavengers, retarders or inhibitors. These substances may be used to determine the rate of production of free radicals.

In the presence of inhibitors, induction periods may be apparent during which virtually no polymerisation takes place, whereas polymerisations carried out in the presence of retarders do not display marked induction periods but proceed at a diminished, although generally changing, rate throughout the course of the reaction. It is generally agreed that both effects result from the interception and removal of the chain carrying free radical. The products of this reaction may be either inert products or new radicals which cannot initiate or propagate the reaction as readily as the original radical species. Since the reactivity of the new radicals relative to that of the original radicals may vary, depending on the nature of the additive, from near unity to approximately zero it is clear that essentially similar mechanisms could operate in both inhibition and retardation.

Possibly the simplest example of the inhibition process is that resulting from the combination of a stable free radical with a polymer radical to produce a stable molecule. An example of this process is the inhibition of styrene [33] and vinyl acetate [34] polymerisation by the stable free radical $\alpha\alpha$-diphenyl-β-picryl hydrazyl (DPPH). However very few free radicals are so stable that

they will not initiate chain reactions to some extent, resulting in a complication in the kinetic picture, e.g. triphenylmethyl can act as both an initiator and retarder of the polymerisation of styrene [35].

With inhibitors and retarders which are not radicals, not only the reaction of the chain carrier with the retarder molecule must be considered but also the subsequent behaviour of the new radicals so formed, and the overall rate of polymerisation may be influenced in several possible ways [36]. The initial attack on the chain carrier by the added species X may be either direct addition to a polymer radical

$$R_n^{\bullet} + X \longrightarrow R_nX^{\bullet} \qquad (6.i)$$

or a transfer reaction such as

$$R_n^{\bullet} + X \longrightarrow P_n + X^{\bullet} \ , \qquad (6.ii)$$

and these new radical species formed may undergo a variety of subsequent reactions with each other or with polymer radicals. The possible reactions include

(1) termination by mutual reaction or by reaction with polymer radicals;

(2) transfer with monomer or, less probably, with the added substance;

(3) Propagation with monomer or, less probably, with the added substance.

The molecules produced by the reactions in (1), (2) and (3) may be inert or may participate further in a variety of ways, including initiation, retardation, transfer and copolymerisation and the mechanism is not complete until the eventual conversion of each radical into a stable molecule has been accounted for.

The termination reaction between metal salts and polymer radicals is akin to reaction (6.ii), and is pertaining to this present work.

KINETICS OF INHIBITED AND RETARDED REACTIONS

For the substance X reacting with polymer radicals directly to give products incapable of further reaction, the simple reaction scheme for vinyl polymerisation may be shown as:

		Rate	
Catalyst	$\longrightarrow 2R_c^{\bullet}$		
$R_c^{\bullet} + M$	$\longrightarrow R_1^{\bullet}$	I	(7.i)
$R_n^{\bullet} + M$	$\longrightarrow R_{n+1}^{\bullet}$	$k_p[R][M]$	(7.ii)
$R_n + X$	$\longrightarrow$ Inert polymer	$k_x[R][X]$	(7.iii)
$R_n^{\bullet} + R_m^{\bullet}$	$\longrightarrow P_{n+m}$ or $P_n + P_m$	$k_t[R]^2$	(7.iv)

Thus

$$\frac{d[R]}{dt} = I - k_x[R][X] - k_t[R]^2 \qquad (8)$$

and

$$-\frac{d[X]}{dt} = k_x[R][X] \qquad (9)$$

where

$$[R] = \sum_n [R_n^{\bullet}]$$

In order to obtain expressions of radical concentrations in terms of experimental variables, it is necessary to assume stationary state conditions and setting $\frac{d[R]}{dt} = 0$. Although the rate of change of radical concentration as reflected in the rate

of change of polymerisation is found, experimentally, to be comparatively large, it is instructive here to apply this simplification

$$\text{As} \quad -\frac{d[M]}{dt} = k_p[M][R] = Rp \text{ say,} \qquad (10)$$

then from equations (8) and (9) we have

$$\frac{d[R]}{dt} = \frac{1}{k_p[M]}\frac{dRp}{dt} = I - \left[k_t[R]^2 - \frac{d[X]}{dt}\right]. \qquad (11)$$

Since Rp is very small during an induction period and since k_p is normally of the order of 10 to 1000 $\text{mole}^{-1}\text{l.sec}^{-1}$, the quantity on the left hand side of equation (11) can be made small compared with both I and the other terms on the right hand side if conditions are suitably chosen, so that the stationary state assumption is in fact reasonable.

In the presence of a strong inhibitor the rate of mutual termination of polymer radicals is small compared with the rate of termination by retarder. This is seen by applying the stationary state assumption to the induction period. For the above scheme we can write

$$I = k_x[R][X] + k_t[R]^2 \qquad (12)$$

When the inhibitor has been used up, $[X]$ is zero and the concentration of polymer radicals attains its maximum value $[R]_s$ given by

$$I = k_t[R]_s^2 \qquad (13)$$

The fraction of the total termination occurring by mutual reaction of polymer radicals during the induction period, is from equation (10)

$$\frac{k_t[R]^2}{I} = \frac{k_t[R]^2}{k_t[R]_s^2} = \frac{Rp^2}{(Rp)_s^2} \quad , \qquad (14)$$

and is sufficiently small to be neglected. Hence, during this period, we may write

$$I = k_x[R][X] = -\frac{d[X]}{dt} \qquad (15)$$

and observation of the initial rate of disappearance of X will, in principle, allow an estimate of the rate of initiation to be made.

Bamford et al.[2] have shown that the kinetic features of the polymerisation of styrene in the presence of ferric chloride in non-aqueous media are entirely consistent with the above scheme in which X is a ferric chloride molecule. They have further shown that for this system the stationary state assumption is a very good approximation throughout the course of the reaction and have carried out a fuller kinetic investigation.

By differentiation of equation (12) and writing $FeCl_3$ for X then

$$\frac{d[FeCl_3]}{dt} = -\frac{I + k_t[R]^2}{k_x[R]^2}\frac{d[R]}{dt} \qquad (16)$$

and since

$$-\frac{(d[FeCl_3])}{dt} = k_x[R][FeCl_3] \quad ,$$

from (12) and (16)

$$-\frac{I + k_t[R]^2}{k_x[R]^2}\frac{d[R]}{dt} = -I + k_t[R]^2 \quad . \qquad (17)$$

After rearrangement and integration this becomes

$$-\frac{[R]_s}{[R]} + \log\frac{[R]_s + [R]}{[R]_s - [R]} = k_x[R]_s t + A \qquad (18)$$

where A is a constant and $[R]_s$ is the final steady radical concentration corresponding to $[FeCl_3] = 0$. If ϕ_t, the reduced rate, is defined as the ratio of the rate at time t to its value when $[FeCl_3] = 0$, then if the monomer concentration is effectively constant $\phi_t = \frac{[R]}{[R]_s}$. Hence from (18)

$$\frac{1}{\phi_o} - \frac{1}{\phi_t} + \log\left(\frac{1-\phi_o}{1+\phi_o}\,\frac{1+\phi_t}{1-\phi_t}\right) = k_x[R]_s t \ , \qquad (19)$$

where ϕ_o is the initial value of ϕ_t and $= \frac{(Ik_t)^{\frac{1}{2}}}{(k_x[FeCl_3]_o)}$.

If $\phi_o \ll 1$, equation (19) may be written

$$\frac{1}{\phi_o} - \frac{1}{\phi_t} + \log\frac{(1+\phi_t)}{(1-\phi_t)} = k_x[R]_s t \qquad (20)$$

By choosing a time t' at which the value of $\phi_t = 0{\cdot}648$, equation (20) reduces to

$$\frac{1}{\phi_o} = k_x[R]_s t'$$

or

$$t' = \frac{[FeCl_3]_o}{I} \qquad (21)$$

This result is general for retarded reactions provided

(a) the initial rate is sufficiently small,

(b) the products derived from the inhibitor do not react

further and

(c) the monomer and catalyst concentrations are effectively constant.

Thus Bamford and co-workers have shown that, when these conditions are satisfied, the value of t' is a more satisfactory measure of the induction period than the usual extrapolation of the linear part of the % polymerisation against time curve to the time axis.

Also, if equation (19) is written in an alternative form:

$$-\frac{1}{\phi_t} + \log\frac{I + \phi_t}{I - \phi_t} = -k_x[R]_s t + A \quad , \qquad (22)$$

then ϕ_t may be plotted against $k_x[R]_s t + A$, and by fitting experimental determinations of ϕ_t to the curve the values of $k_x[R]_s$ may be found. Since this is equal to $k_x(I/k_t)^{\frac{1}{2}}$, then $k_x/k_t^{\frac{1}{2}}$ or alternatively k_x/k_p can be calculated.

If the reactions are merely retarded by the metal salt the determination of k_x/k_p is simplified. At salt concentrations sufficiently high to eliminate bimolecular termination, the following equations hold

$$-\frac{d[M]}{dt} = \frac{k_p[M]I}{k_x[FeCl_3]} \qquad (23)$$

$$-\frac{d[FeCl_3]}{dt} = \frac{d[FeCl_2]}{dt} = I \quad , \qquad (24)$$

thus I and k_x/k_p may be estimated readily. This procedure is unsuitable for inhibited reactions because the concentrations of

ferric chloride required are so low that they cannot be regarded as constant during a single experiment.

Bartlett and Kwart [34] have also successfully applied the stationary state approximation to a similar reaction scheme. They have studied the behaviour of various retarders on the polymerisation of vinyl acetate initiated by peroxide catalyst at 45°C, and measured the value of k_x/k_p for the various retarders by means of a kinetic analysis.

A number of kinetic schemes have been proposed to account for more complex reaction schemes for inhibited polymerisation. For example, Kice [37,38] has proposed a scheme in which other possible reactions of the inhibitor molecules or radicals are taken into account and has successfully applied his scheme to the retarded polymerisations of methyl methacrylate [37] and methyl acrylate [38].

If the reaction between the added terminator X with a polymer radical R• leads to the formation of a new radical X•, then the kinetic scheme may be represented as

Initiation	$\longrightarrow$	R•	Rate = I	(25.i)
R• + M	$\longrightarrow$	R•	k_p	(25.ii)
R• + X	$\longrightarrow$	X•	k_x	(25.iii)
X• + M	$\longrightarrow$	R•	k_o	(25.iv)
X• + R•	$\longrightarrow$	Inert products	k_c	(25.v)
X• + X•	$\longrightarrow$	Inert products	k_z	(25.vi)
R• + R•	$\longrightarrow$	Inert products	k_t	(25.vii)

By rigorous kinetic analysis Kice obtained the equation

$$\frac{\mu^2[X]}{1-\mu^2}\left[1+\left\{1+\frac{(1-\mu^2)}{\theta^2\mu^2}\right\}^{\frac{1}{2}}\right] = \frac{k_t R_p}{k_p k_x}\left\{1+\frac{(1-\mu^2)}{\theta^2\mu^2}\right\}^{\frac{1}{2}} \quad \frac{k_t k_o[M]}{k_x k_c}$$

where $\mu = Rp/Ro$ and $\theta = k_c/(k_t k_z)^{\frac{1}{2}}$; Rp and Ro are the rates of polymerisation in the presence and absence of terminator respectively. A plot of

$$\frac{\mu^2[X]}{1-\mu^2}\left[1+\left\{1+\frac{(1-\mu^2)}{\theta^2\mu^2}\right\}^{\frac{1}{2}}\right] \text{ versus } Rp\left\{1+\frac{(1-\mu^2)}{\theta^2\mu^2}\right\}^{\frac{1}{2}}$$

for various runs with a given terminator should be a straight line of slope $k_t/k_p k_x$ and intercept $k_t k_o[M]/k_x k_c$. If values of k_t and k_p for the polymerisation are known and assuming the 'best value of θ' [37], then values of k_x and k_o/k_c for the terminator may be obtained.

More recently Bamford et al.[4] have taken into account the possible reactions of the primary radicals derived from the initiator, in the ferric chloride terminated polymerisations of acrylonitrile, methacrylonitrile, methyl methacrylate and methyl acrylate. The reaction scheme includes all the reactions in (7) together with the termination reactions of primary radicals with polymer radicals, ferric chloride molecules and by mutual reaction. A kinetic analysis has enabled the rate constants for the reactions during polymerisations to be evaluated. The results show the rate of initiation is independent of the nature of the monomer, the mean value obtained for $2k_i$ being $1{\cdot}39 \times 10^{-5}$ sec.$^{-1}$ with a maximum deviation from this of only 4·3%. The values obtained for k_x, the rate constant for the reaction between ferric chloride and polymer radicals, are close to those calculated from the

simpler scheme, where primary radical termination was not taken into account [3].

KINETIC ANALYSIS USED IN PRESENT STUDIES.

From the reaction scheme (7) (page 15) in which X is $CuCl_2$ or $CuBr_2$, we obtain equation (22)

$$-\frac{1}{\phi_t} + \log\frac{1+\phi_t}{1-\phi_t} = k_x[R]_s t + A$$

A plot of the left hand side of equation (22) against t gives a line of slope equal to $k_x[R]_s$, and since

$$\frac{k_x}{k_p} = \frac{k_x[R]_s[M]}{(Rp)_s} \quad , \qquad (26)$$

the value of k_x/k_p may be determined.

An alternative method of determining k_x/k_p may be developed from the kinetics in the following way. Assuming that at any time t a stationary radical concentration $[R]_t$ exists and is defined by

$$\frac{d[R]_t}{dt} = I - k_x[R]_t[CuCl_2] - k_t[R]_t^2 = 0, \qquad (27)$$

whence

$$[R]_t = -\frac{k_x[CuCl_2]}{2k_t} + \frac{(k_x^2[CuCl_2]^2 + 4Ik_t)^{\frac{1}{2}}}{2k_t} \qquad (28)$$

The final radical concentration when the cupric salt concentration

has fallen to zero therefore $= (I/k_t)^{\frac{1}{2}}$. Thus

$$\phi_t = \frac{[R]_t}{[R]_s} = \left[\frac{(k_x^2[CuCl_2]^2 + 4Ik_t)^{\frac{1}{2}} - k_x[CuCl_2]}{2(Ik_t)^{\frac{1}{2}}}\right] \qquad (29)$$

Rearranging and squaring we obtain

$$k_x = \frac{\left\{(1 - \phi_t^2)/\phi_t\right\}(Ik_t)^{\frac{1}{2}}}{[CuCl_2]} \qquad (30)$$

A variation in $[CuCl_2]$ with % polymerisation is determined as follows:

$$-\frac{d[CuCl_2]}{dt} = k_x[R]_t[CuCl_2] \ ,$$

i.e.,

$$-\frac{1}{k_x}\int_{[CuCl_2]_o}^{[CuCl_2]} \frac{d[CuCl_2]}{[CuCl_2]} = \int_o^t [R]_t dt \ . \qquad (31)$$

But

$$\int_o^t [R]_t dt = -\frac{1}{k_p}\int_{[M]_o}^{[M]} \frac{d[M]}{[M]} \ . \qquad (32)$$

Equating (31) and (32) and integrating gives

$$(k_p/k_x)\ \ln\left([CuCl_2]/[CuCl_2]_o\right) = \ln\left([M]/[M]_o\right) \qquad (33)$$

where $[CuCl_2]_o$, $[M]_o$ and $[CuCl_2]$, $[M]$ are the cupric salt and monomer concentrations initially and at time t respectively.

Rearranging equation (33),

$$[CuCl_2] = [CuCl_2]_o([M]/[M]_o)^{k_x/k_p}$$

$$= [CuCl_2]_o(1 - F)^{k_x/k_p} \quad , \qquad (34)$$

where F is the fractional conversion of monomer to polymer.

Substituting from equation (34) in equation (30),

$$k_x = \frac{\left\{(1 - \phi_t^2)/\phi_t\right\} (\Pi k_t)^{\frac{1}{2}}}{[CuCl_2]_o(1 - F)^{k_x/k_p}} \qquad (35)$$

The value of k_x/k_p can be determined from the slope of the line

The value of k_x/k_p can be determined from the slope of the line $[CuCl_2]_o^{-1}$ against the logarithm of (1 - F) for fixed values of the remaining two variables.

ADDITIONAL TERMINATION REACTIONS.

In the derivations so far considered, the products of the termination reaction between polymer radicals and cupric chloride do not react further.

If we now consider the kinetics involved where the products of the inhibition reaction (cuprous chloride or some complex with solvent, monomer or polymer) react with polymer radicals to retard the polymerisation.

The reactions involved can be represented by the following kinetic scheme.

			Rate	
Initiation	AIBN	$\longrightarrow 2R_c^{\bullet}$		
	$R_c^{\bullet} + M$	$\xrightarrow{k_i} R^{\bullet}$	I	
Propagation	$R_n^{\bullet} + M$	$\xrightarrow{k_p} R_{n+1}^{\bullet}$	$k_p[R][M]$	(36.ii)
Termination	$R_n^{\bullet} + CuCl_2$	$\xrightarrow{k_x}$ CuCl + polymer	$k_x[R][CuCl_2]$	(36.iii)
	$R_n^{\bullet} + CuCl$	$\xrightarrow{k_y}$ polymer	$k_y[R][CuCl]$	(36.iv)
	$R_n^{\bullet} + R_m^{\bullet}$	$\longrightarrow$ polymer	$k_t[R]^2$	(36.v)

Since cupric chloride is an inhibitor in the present system, reaction (36.iii) must overwhelm the other termination reactions during the inhibition period. When all the cupric chloride has been removed and polymerisation commences, termination can occur either by reaction (36.iv) or (36.v) depending upon the concentration of cuprous chloride in the system. If termination occurs exclusively by reaction (36.v), then the system behaves as that described in reaction scheme (7) and the rate is given from equations (10) and (13) by

$$\text{Rate} = \frac{k_p I^{\frac{1}{2}}[M]}{k_t^{\frac{1}{2}}} \qquad (37)$$

If termination occurs enclusively by reaction (36.iv), then the rate of polymerisation, R_p, will be given by equation (38).

$$R_p = \frac{k_p I[M]}{k_y[CuCl]} \qquad (38)$$

Now considering the latter case, with the mutual bi-radical

termination as negligible, and assuming that a stationary state radical concentration $[R]_t$ exists and is defined by

$$\frac{d[R]_t}{dt} = I - k_x[R]_t[CuCl_2] - k_y[R]_t[CuCl] = 0 \qquad (39)$$

Now

$$[CuCl_2] = [CuCl_2]_o - [CuCl] \qquad (40)$$

Therefore from (39) and (40) we have

$$0 = I - (k_x - k_y)[R]_t[CuCl_2] - k_y[R]_t[CuCl_2]_o \qquad (41)$$

which by rearrangement gives

$$[CuCl_2] = \frac{\left\{(I/[R]_t) - k_y[CuCl_2]_o\right\}}{(k_x - k_y)} \qquad (42)$$

Now cupric chloride is removed from the system by reaction (36.iii), hence

$$-\frac{d[CuCl_2]}{dt} = k_x[R]_t[CuCl_2] \qquad (43)$$

Differentiating (42) with respect to t and equating with (43) we get

$$\left\{I/[R]_t^2\right\} d[R]/dt = k_x\left\{I - k_y[R]_t[CuCl_2]_o\right\} \qquad (44)$$

At the end of the period of inhibition and acceleration when all the cupric chloride has been consumed let the steady state radical concentration be $[R]_y$ where

$$[R]_y = \frac{I}{k_y[CuCl_2]_o} \qquad (45)$$

and let $\phi' = [R]_t/[R]_y$ where $[R]_t$ is the radical concentration after time t at an earlier stage of the reaction.

Integrating (44) and replacing $[R]_t/[R]_y$ by ϕ' we obtain the following equation

$$-\frac{1}{\phi'} - \ln\left\{\frac{(1-\phi')}{\phi'}\right\} = k_x[R]_y t + \text{constant} \qquad (46)$$

Substituting the limits of integration when

$t = 0$, $\phi' = \phi'_o$ and when $\phi' = 1$, $[CuCl_2] = 0$

equation (46) becomes

$$\frac{1}{\phi'_o} - \frac{1}{\phi'} + \ln\left\{\frac{\phi'(1-\phi'_o)}{\phi'_o(1-\phi')}\right\} = k_x[R]_y t \qquad (47)$$

Equation (47) may be compared with equation (19) which was obtained by Bamford et al.[2] for a system in which termination occurred by reactions (36.iii) and (36.v).

$$\frac{1'}{\phi_o} - \frac{1}{\phi} + \ln\left\{\frac{(1-\phi_o)(1+\phi)}{(1+\phi_o)(1-\phi)}\right\} = k_x[R]_s t \qquad (19)$$

As described earlier (page 23) a solution may be obtained giving a time t', at which ϕ equals 0·648, which enables the value of I to be calculated. Unfortunately no similar solution from equation (47) is possible since no single value of ϕ' will give an equation similar to (21).

A measure of the rate of initiation, however, may be obtained from the intercept of the extrapolated linear portion of the conversion against time curve with the time axis. The value of this intercept may be obtained by the following procedure used by Bamford for the ferric chloride system.

Let curve 'a' in fig. 1 represent the period of acceleration to the steady retarded rate following inhibition, and line 'b' be a straight line drawn through the origin parallel to the linear portion of curve 'a'. Let the vertical distance between curve 'a' and line 'b' be equal to Δ, and Δ_y be the value of Δ when curve 'a' becomes linear. Δ is given by

$$\Delta = k_p[M]\int_0^t ([R]_y - [R])dt \qquad (48)$$

Differentiating equation (12) we get

$$k_x[R]_y dt = d\phi'/\phi'^2(1-\phi') \qquad (49)$$

i.e.

$$k_x\Delta = k_p[M]\int_{\phi_o'}^{\phi'} d\phi'/\phi'^2 \qquad (50)$$

When ϕ' becomes equal to unity, Δ becomes equal to Δ_y.

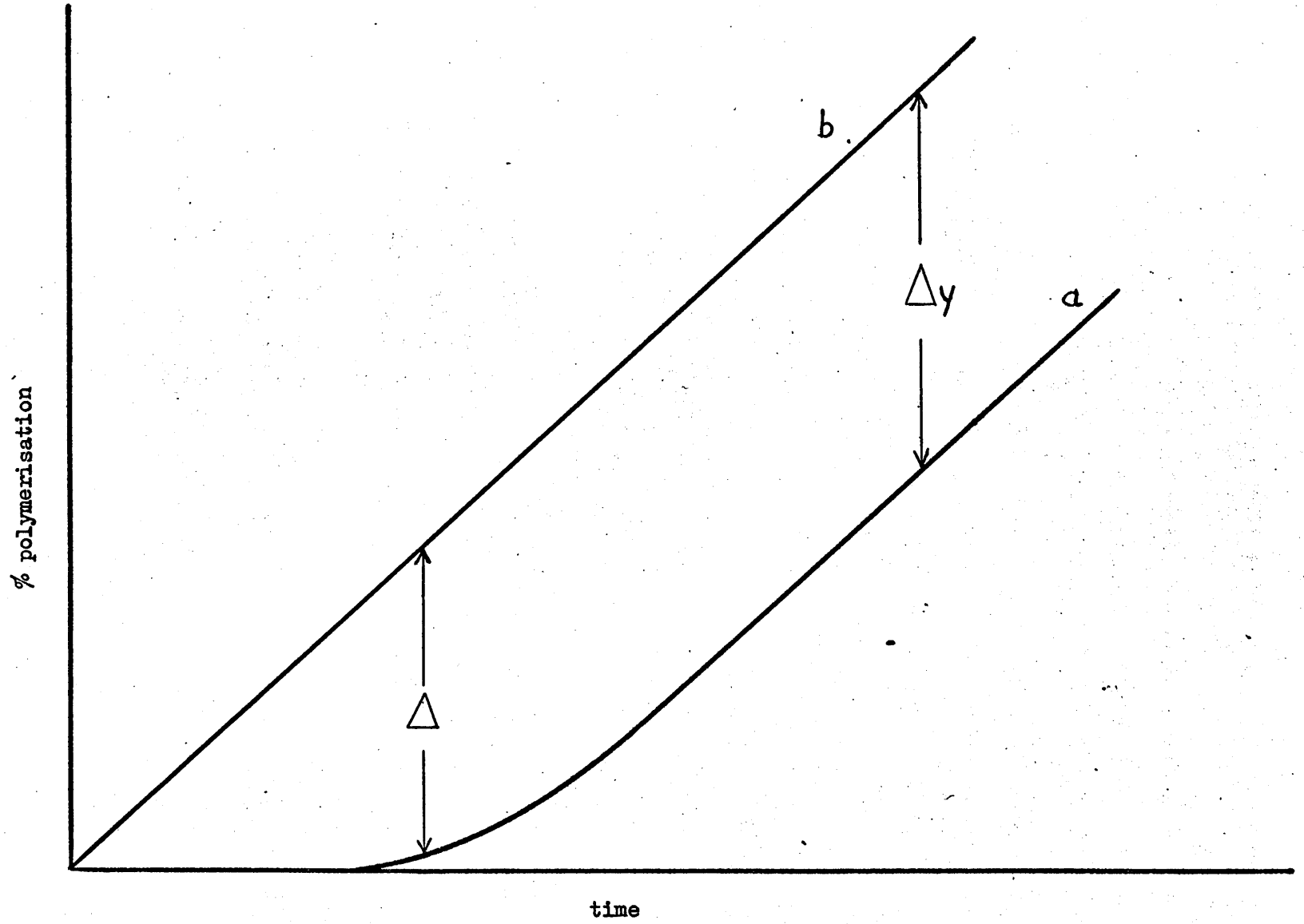
Therefore by integrating equation (50) between ϕ_o' and 1 we get

$$\Delta_y = k_p[M]\{(1/\phi_o')-1\}/k_x \qquad (51)$$

now

$$\Delta_y/\text{intercept OA} = k_p[M][R]_y \qquad (52)$$

Fig. 1 A conversion against time plot showing the significance of Δ



Substitute for Δ_y from equation (51) and rearrange, we get

$$\text{intercept OA} = \left\{1-(k_y/k_x)\right\}[CuCl_2]_o/I \qquad (53)$$

Thus values for the rates of initiation in this system calculated from the intercept of the extrapolated retarded rate of polymerisation to the time axis should be corrected by multiplying by the factor $\left\{1-(k_y/k_x)\right\}$. The value of k_y/k_p may be obtained from equation (38), and the value of k_x/k_p may be obtained using equation (46). The plot of the l.h.s. of equation (46) against t should be a straight line with gradient equal to $k_x[R]_y$. The value of the ratio k_x/k_p may then readily be obtained by substituting the appropriate values in equation (54).

$$\frac{k_x}{k_p} = \frac{k_x[R]_y[M]}{(-d[M]/dt)_y} \qquad (54)$$

An alternative method of determining k_x/k_p may be obtained from the kinetics in the following way.

Rearranging equation (41) we get

$$[R]_t = \frac{I}{\left\{(k_x-k_y)[CuCl_2] + k_y[CuCl_2]_o\right\}} \qquad (55)$$

Substituting for I from equation (45) and replacing $[R]_t/[R]_y$ by ϕ', equation (55) becomes,

$$\phi' = \frac{k_y[CuCl_2]_o}{\left\{(k_x-k_y)[CuCl_2] + k_y[CuCl_2]_o\right\}} \qquad (56)$$

From equation (34) we have

$$[CuCl_2] = [CuCl_2]_o (1-F)^{k_x/k_p} \qquad (34)$$

Combining (56) and (34) we have

$$\frac{k_x}{k_y} - 1 = \frac{\left\{(1/\phi') - 1\right\}}{(1 - F)^{k_x/k_p}}$$

Thus the plot of $\log \left\{(1/\phi')-1\right\}$ against $\log (1-F)$ should be a straight line of gradient k_x/k_p.

No simple solution for valuating k_x and k_y could be obtained for the reaction where mixed order termination occurs (i.e. contribution from both reactions (36.iv) and (36.v)).

EXPERIMENTAL

MATERIALS

Acrylonitrile (AN) was obtained from B.D.H. Ltd., dried over anhydrous calcium chloride for at least one day, filtered and distilled at atmospheric pressure. The fraction boiling at 77.3°C was collected.

Methyl Methacrylate (MM) was obtained from I.C.I. Ltd., freed from inhibitor by washing with dilute aqueous sodium carbonate solution followed by distilled water. It was dried over anhydrous calcium chloride for at least 24 hours, the calcium chloride being changed several times, filtered and then distilled under nitrogen.

The final purification is similar for both monomers. Immediately before use, the monomer was transferred to a distillation flask which was connected to the high vacuum line and the solution was thoroughly 'degassed' by several 'trap-to-trap' distillations. It was finally distilled 'in vacuo' into a flask containing a little AIBN and prepolymerised photochemically to about 10% conversion. The unreacted monomer was distilled off at room temperature to a reservoir flask, on the vacuum line, and kept under vacuum at -78°C.

1,1'-azo-bis-isobutyronitrile (AIBN) was obtained from Kodak, Ltd., and purified by recrystallizing twice from absolute ethanol (m.p. 102°C). To avoid decomposition, care was taken not to heat the solution above 30°C during purification. It was found convenient to add the AIBN in the form of a standard chloroform

solution, and these solutions were stored in darkness and were discarded after one week.

Cupric Salts. A.R. grades of $CuCl_2$, $CuBr_2$, $Cu(NO_3)_2 \cdot 3H_2O$ and $(CH_3COO)_2Cu.H_2O$ were used without further purification.

Dimethylformamide (DMF) was obtained from B.D.H. Ltd., purified by five one-hour treatments with phosphorous pentoxide, filtered and distilled at atmospheric pressure; the fraction boiling at 153°C was collected. This fraction was finally distilled 'in vacuo'.

Methyl Cyanide was obtained from B.D.H. Ltd., treated with phosphorous pentoxide and distilled at atmospheric pressure.

APPARATUS

High Vacuum Line. This consisted of a series of traps and vacuum tested taps (4mm. bore) in Pyrex glass connected via a mercury vapour diffusion pump to a rotary oil pump. Apiezon high vacuum grease was used for the taps. Cold traps were placed before and after the mercury diffusion pump, the coolant used in these traps and as the receiver coolant for distillation on the line was a solid carbon dioxide - acetone mixture.

The vacuum was tested by a Pirani gauge and all vessels fitted to the line were checked for air leaks by observing the discharge obtained from a high voltage coil (Tesla coil) activated close to the line. With this system a vacuum of 10^{-4}mm.Hg could easily be obtained.

Thermostatically Controlled Tank. All polymerisation experiments were carried out under standard conditions in a

cylindrical glass tank. This was surrounded by an aluminium jacket with an observation window, and the annular space between the tank and jacket was filled with asbestos wool lagging. The capacity of the tank was about 25 litres. Heat was supplied by a Variac controlled 2 kw. circular element heater, and a constant temperature was maintained by a relay operated filament heater (50W), the relay circuit being actuated by a mercury-toluene regulator. Other contents were a stirrer, a dilatometer stand, and a 15 amp. observation lamp, suspended in a tubular glass vessel, situated behind the dilatometer stand.

Reaction Vessels. All polymerisation reactions were carried out in vacuum tested Pyrex glass dilatometers. These were of three types and may be categorised according to their use as follows:-

1. Those used in the preliminary investigations and for measurements of inhibition periods by the extrapolation technique. For methyl methacrylate studies the bulb capacity was 3 - 4 ml. and 7 - 8ml. for acrylonitrile polymerisations. In both cases the capillary consisted of veridia tubing of 1mm. diameter.
2. For studies of the acceleration periods in the cupric chloride inhibited polymerisation of methyl methacrylate the dilatometers had a bulb capacity of approximately 11ml. with 1mm. capillary stems.
3. For studies of the acceleration periods in the cupric bromide inhibited polymerisation of methyl methacrylate the dilatometers had flattened bulbs,

approximately 5 cm. in diameter and 0 5 cm. thick, with Veridia tubing of 0·8mm. diameter. This shape is essential in this system to maintain, as near as possible, isothermal conditions.

PROCEDURE

All inhibition and polymerisation experiments were carried out in dilatometers sealed 'in vacuo'. The dilatometers were calibrated by adding Analar acetone from a burette reading to 0·02ml.. AIBN was introduced into the calibrated dilatometer in standard chloroform solution and the solvent pumped off. The required amount of cupric salt was added in DMF solution, and additional DMF added where necessary to achieve the required concentration of the latter in the final solution. The dilatometer was then attached to the high vacuum line, and the solution outgassed by repeatedly freezing, pumping and thawing. Finally, monomer was distilled from the reservoir vessel to a calibrated vessel, from which the required quantity was distilled to the dilatometer which was then sealed off with a flame. The dilatometers were immersed in the water thermostat at the required temperature, and the polymerisations were followed by the meniscus movement of the monomer solution. In all cases the contraction was followed by means of a cathetometer, but modified techniques had to be employed to enable a sufficiently high degree of accuracy in the measurements.

In the initial experiments where measurement of inhibition periods, by extrapolation of the final rate to the time axis, was required, the normal method of measuring contraction

at time intervals of several minutes was used. For detailed examination of the elbow part of the curve from which values of the reduced rate, ϕ_t, have to be measured, different techniques had to be employed for the different salts. For the inhibition of the polymerisation of methyl methacrylate by cupric chloride, ϕ_t increases from approximately 0·1 to 0·9 during a time interval of 4 - 6 minutes. Thus contraction readings taken at every $\frac{1}{2}$ or 1 minute intervals enables an accurate plot to be made of fractional conversion versus time for this part of the curve. Using a tape recorder, with a recording of a 'count-down' every $\frac{1}{2}$ minute during the experiment, accurate cathetometer readings could be taken at these time intervals. With cupric bromide, however, for the same limits of ϕ_t the time interval is less than 3 minutes, and a method has been used to obtain readings at much more frequent intervals. Using a cathetometer fitted with an eyepiece scale of 100 divisions, times of meniscus movement past each division were recorded on an Elliot pen recording voltmeter with a chart speed of 12 inches per minute, by means of a release switch. Two gratings (A & C) were used in the experiments and these enabled each contraction of 0·0241cm. and 0·015cm. respectively to be recorded.

In order to obtain the relationship between contraction and conversion, the polymer was precipitated at known fractional contractions and the corresponding fractional conversion obtained by weighing the isolated polymer. The precipitation experiments were carried out as follows.

The dilatometers were filled as described and placed in the thermostatically controlled tank at 60°C. At the required fractional contraction the dilatometer was removed from the tank

and the contents frozen with liquid nitrogen. The dilatometer was then opened and the contents thawed. With polyacrylonitrile the contents were added slowly to a tenfold excess of methanol which was vigorously stirred during the addition. The dilatometer was washed out thoroughly with DMF and the washings added to the methanol solution. The precipitated polymer was then filtered, washed and dried 'in vacuo' at 60°C to constant weight. With polymethyl methacrylate the thawed contents of the dilatometer were added to acetone and the dilatometer thoroughly rinsed out with the latter. The acetone solution was then added very slowly to a large excess of 10% aqueous methanol which was vigorously stirred during the precipitation. The polymer was then filtered, washed and dried as before.

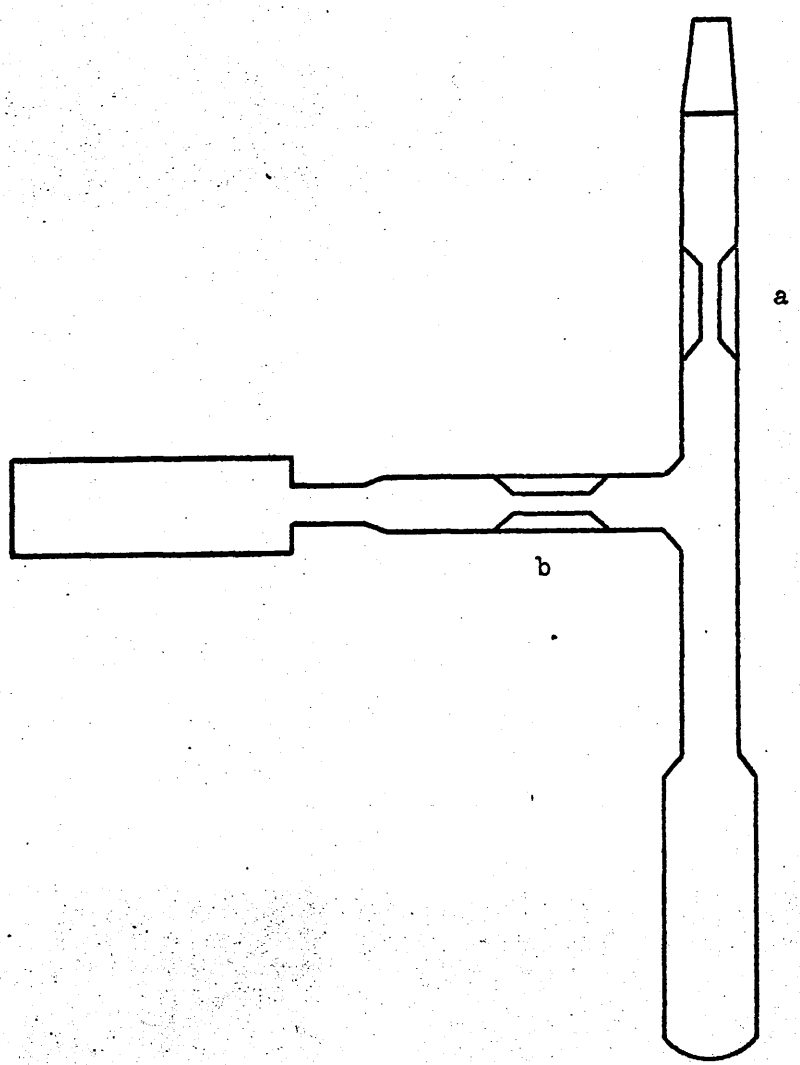
SPECTROPHOTOMETRIC MEASUREMENTS

All absorption measurements were made using a Perkin Elmer spectrophotometer (Model UV 137), with a thermostat fitted to enable changes in optical density to be measured at 60°C.

The absorption cells (1cm.) were filled in a similar manner to the dilatometers on the high vacuum line, the AIBN and cupric chloride - DMF solution being added as before. To avoid damage to the cell, the solution was outgassed in a Pyrex bulb fitted to the cell, shown in fig. 2. The required quantity of monomer was distilled into the bulb and the vessel isolated by sealing off at constriction 'a'. The contents of the bulb were then heated to room temperature and poured into the cell which was isolated by sealing off at constriction 'b'.

The cell was placed in the thermostat in the

Fig.2 Reaction Vessel for Spectrophotometric Measurements



spectrophotometer together with a 'blank' cell containing the same concentration of monomer and solvent, and the optical density measured at intervals of several minutes.

R E S U L T S

SECTION 1 - THE POLYMERISATION OF ACRYLONITRILE IN THE PRESENCE OF CUPRIC CHLORIDE

CONVERSION FACTOR

A linear relationship between the fractional contraction V/Vo and the fractional conversion F was found to hold over the first 10% polymerisation.

For acrylonitrile polymerisation at 60°C

$$V/Vo = 0{\cdot}297 \times F$$

This relationship differs significantly from the expected conversion factor of 0·375 calculated from the density data of monomer and polymer in DMF at 60°C, but lies within the range of values 0·27 to 0·32 calculated from monomer and polymer density data at 25°C[39,40].

THE EFFECT OF CUPRIC CHLORIDE ON THE POLYMERISATION OF ACRYLONITRILE INITIATED BY AIBN.

All reactions were carried out at 60°C, the AN - DMF proportion being held constant at 20% - 80% by volume such that $[M] = 2{\cdot}87$ mole $l.^{-1}$. This ensures that the system remains homogeneous throughout the reaction thus avoiding complications associated with polymer precipitation. The $[AIBN]/[CuCl_2]$ was

maintained at a high value to ensure that the AIBN concentration, and consequently the rate of initiation, remained substantially constant throughout the period of inhibition and that the post-inhibition rate of polymerisation would be expected to have the same value as that in the absence of cupric chloride.

Initially the effect of cupric chloride on the polymerisation of AN, initiated by $1{\cdot}0 \times 10^{-2}$ mole $l.^{-1}$ was studied. Fig. 3 refers to polymerisation against time curves for reactions carried out in the presence of from $2{\cdot}14 \times 10^{-4}$ to $1{\cdot}36 \times 10^{-3}$ molar cupric chloride.

In each case the polymerisation is inhibited, the inhibition period increases while the rate of polymerisation decreases with increase in the initial cupric chloride concentration. During the inhibition period the cupric chloride colour fades gradually, disappearing by the end of the inhibition, then it intensifies during the retarded rate of polymerisation to a final yellow colour.

Similar plots to those in fig. 3 were obtained with higher AIBN and $CuCl_2$ concentrations. In fig. 4 the inhibition period obtained by extrapolating the linear portion of the conversion against time curves to zero conversion is plotted against the initial cupric chloride concentration ($[CuCl_2]_o$). The results for both AIBN concentrations lie on straight lines which pass through the origin, indicating no inhibition in the absence of cupric chloride. Zero time for all these experiments was taken when the meniscus in the dilatometer had risen to its maximum height (about 4 minutes after immersing it in water

Fig.3 The effect of cupric chloride on the polymerisation of acrylonitrile.

$[AIBN] = 1 \times 10^{-2}$ mole $l.^{-1}$.

$[CuCl_2]_o =$ 0, 2·14, 3·55, 5·63, 7·58, 10·67 and 13·57 $\times 10^{-4}$ mole $l.^{-1}$ for curves a - g respectively.

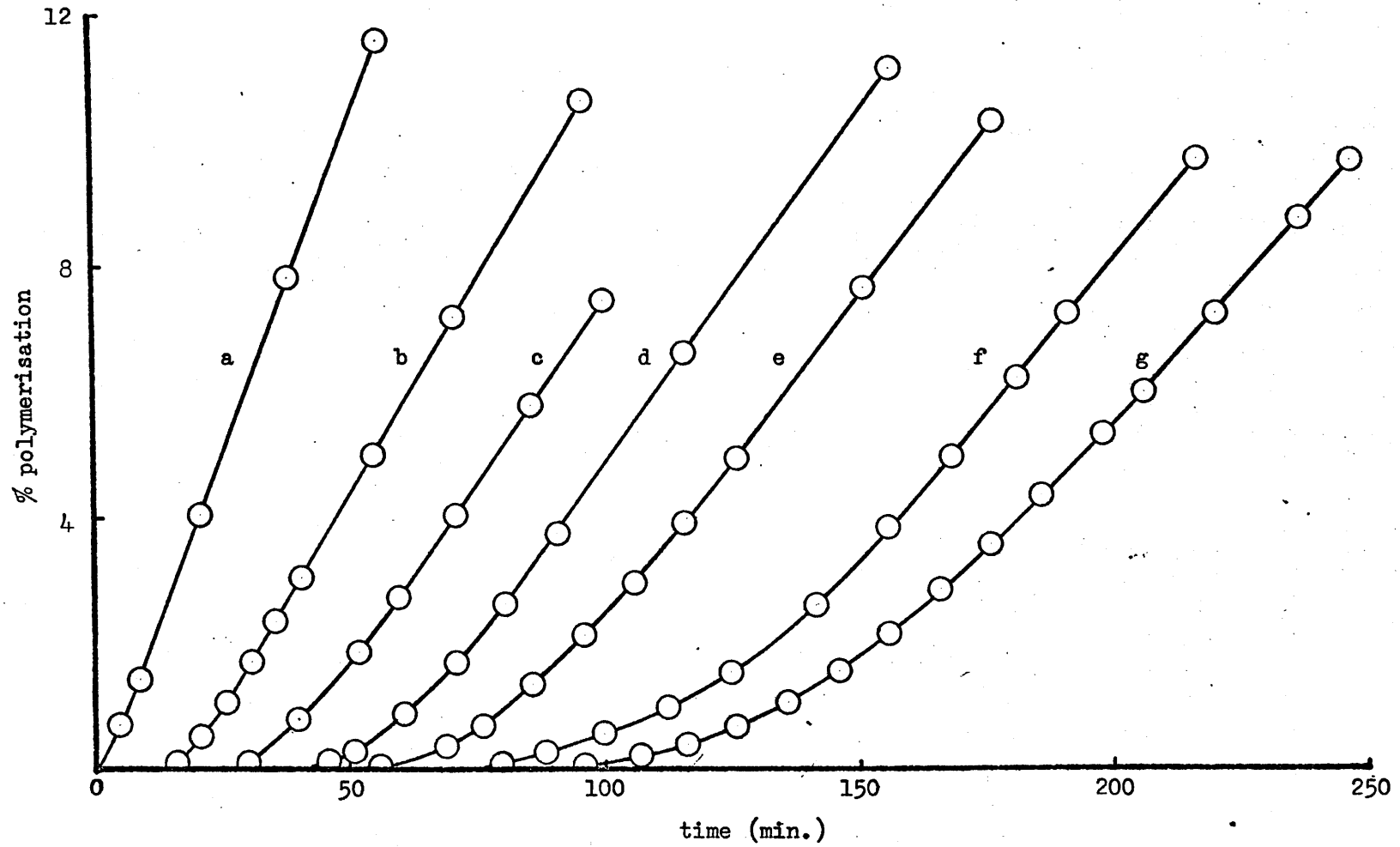
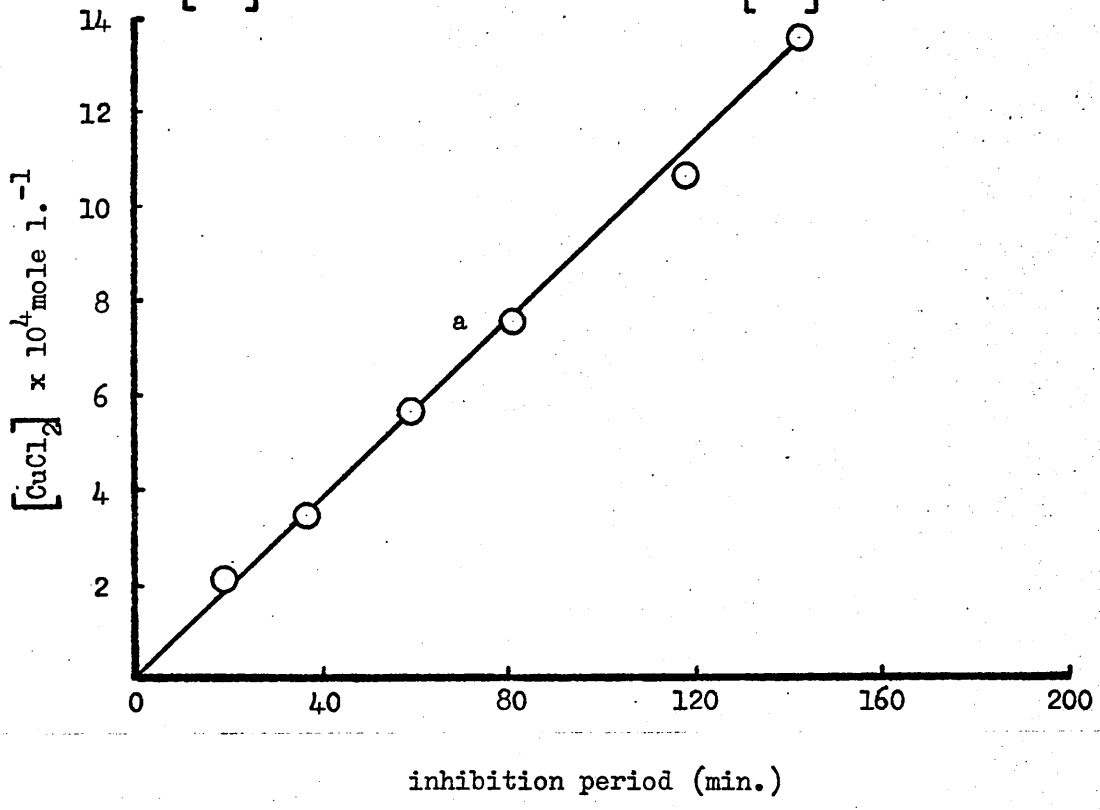
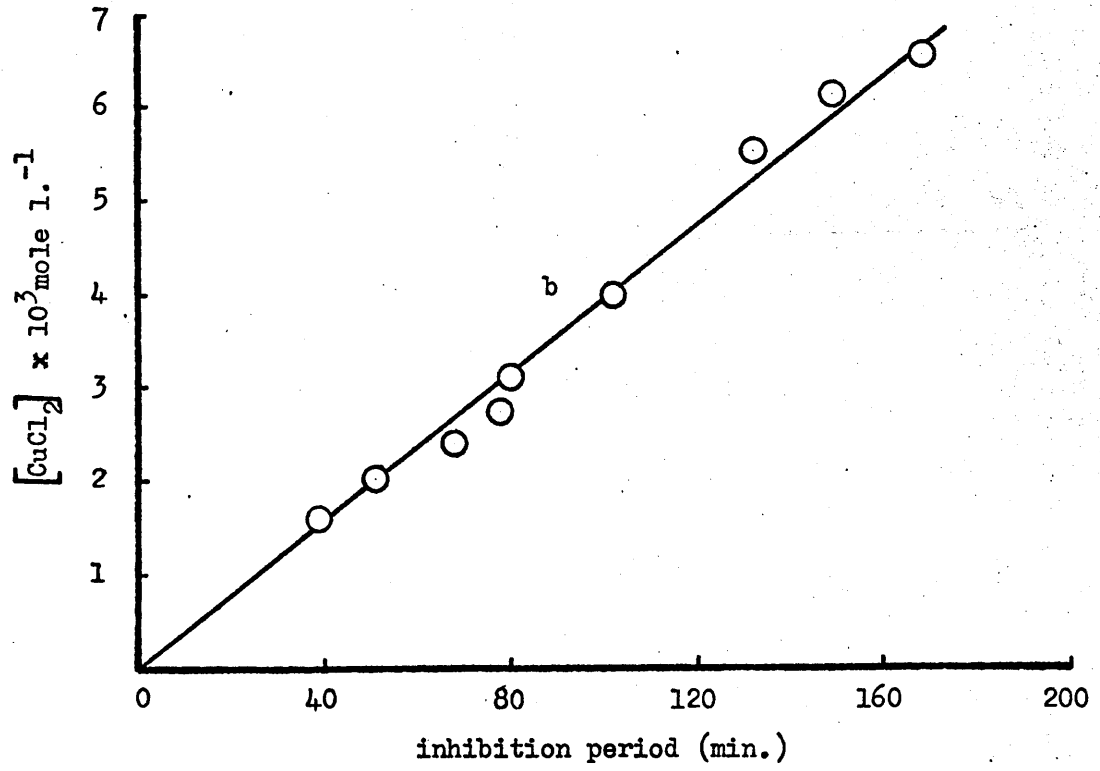


Fig.4 The effect of cupric chloride on the inhibition period for the polymerisation of acrylonitrile.

a. $[AIBN] = 1 \times 10^{-2}$ mole $l.^{-1}$. b. $[AIBN] = 4 \times 10^{-2}$ mole $l.^{-1}$.





thermostat). If it is assumed that each initiating radical reacts with one molecule of cupric chloride then the rate of removal of cupric chloride is equal to the rate of initiation (I).

The values obtained from the slopes in fig. 3 are:-

$-d[CuCl_2]/dt$	$[AIBN]$	$2k_i$
mole $l^{-1}s^{-1}$	mole l^{-1}	s^{-1}
$1{\cdot}59 \times 10^{-7}$	$1{\cdot}0 \times 10^{-2}$	$1{\cdot}59 \times 10^{-5}$
$6{\cdot}52 \times 10^{-7}$	$4{\cdot}0 \times 10^{-2}$	$1{\cdot}63 \times 10^{-5}$

The degree of retardation increases with increasing initial cupric chloride concentration and values obtained for an $[AIBN]$ of $4{\cdot}0 \times 10^{-2}$ mole l^{-1} and $[CuCl_2]_o$ from 2·02 to $6{\cdot}55 \times 10^{-3}$ mole l^{-1} are listed in Table 1.

Table 1. - Dependance of retarded rate of polymerisation on initial cupric chloride concentration.

$[AIBN] = 4 \times 10^{-2}$ mole l^{-1}

$[CuCl_2]_o$	Retarded Rate	Retarded Rate x $[CuCl_2]_o$
x 10^3 mole l^{-1}	x 10^5 mole $l^{-1}sec^{-1}$	x 10^7 mole^2 $l^{-2}sec^{-1}$
2·02	13·4	2·72
2·40	12·5	3·00
2·75	11·1	3·06
3·11	9·46	2·94
3·97	8·02	3·18
5·53	6·29	3·48
6·13	4·87	2·99
6·55	4·67	3·06

The results obtained from reactions carried out at various initial catalyst concentrations are summarised in Table 2. Since a fraction of the catalyst decomposes during the inhibition period a correction has been applied using the value[26] of $1 \cdot 01 \times 10^{-5} s^{-1}$ for k_d, the rate of decomposition of AIBN in DMF at 60°C. In Table 2, $[AIBN']$ refers to the catalyst concentration at the end of the inhibition period and $[\overline{AIBN}]$, the average catalyst concentration during the inhibition period.

Table 2 /-

Table 2. - Dependence of inhibition period and retarded rate of polymerisation on AIBN concentration.

$[CuCl_2]_o$ = $9{\cdot}04 \times 10^{-4}$ mole $l.^{-1}$.

$[AIBN]$ $\times 10^2$ mole $l.^{-1}$	Inhibition Period $T \times 10^{-3}$ sec	Retarded Rate $\times 10^5$ mole $l.^{-1}$ sec^{-1}	$T \times [\bar{AIBN}]$ $\times 10^{-1}$	$\frac{\text{Retarded Rate}}{[AIBN']^{-}}$ $\times 10^3$	$\frac{\text{Retarded Rate}}{[AIBN']^{\frac{1}{2}}}$ $\times 10^4$
0.5	11.76	2.96	5.53	6.71	4.05
1	5.28	5.60	5.14	5.91	5.76
2	2.40	9.28	4.74	4.76	6.63
4	1.08	16.4	4.29	4.16	8.25
		$[CuCl_2]_o$ = $1{\cdot}6 \times 10^{-3}$ mole $l.^{-1}$.			
1	10.44	4.48	9.89	5.00	4.74
2	4.86	8.64	9.48	4.55	6.26
3	3.30	11.5	9.74	3.97	6.76
4	2.34	15.0	9.24	3.84	7.58

Thus the results are in accordance with reaction scheme (36), with the length of the induction period being proportional to $[CuCl_2]_o$ and inversely proportional to $[AIBN]$. The retarded rate following inhibition is proportional to $[AIBN]^x$ where $1<x>0.5$, indicating both first and second order termination reactions are occurring. The results in Table 1 suggest that first order termination may be predominant at high $[CuCl_2]_o$.

RATE CONSTANTS OF TERMINATION REACTION.

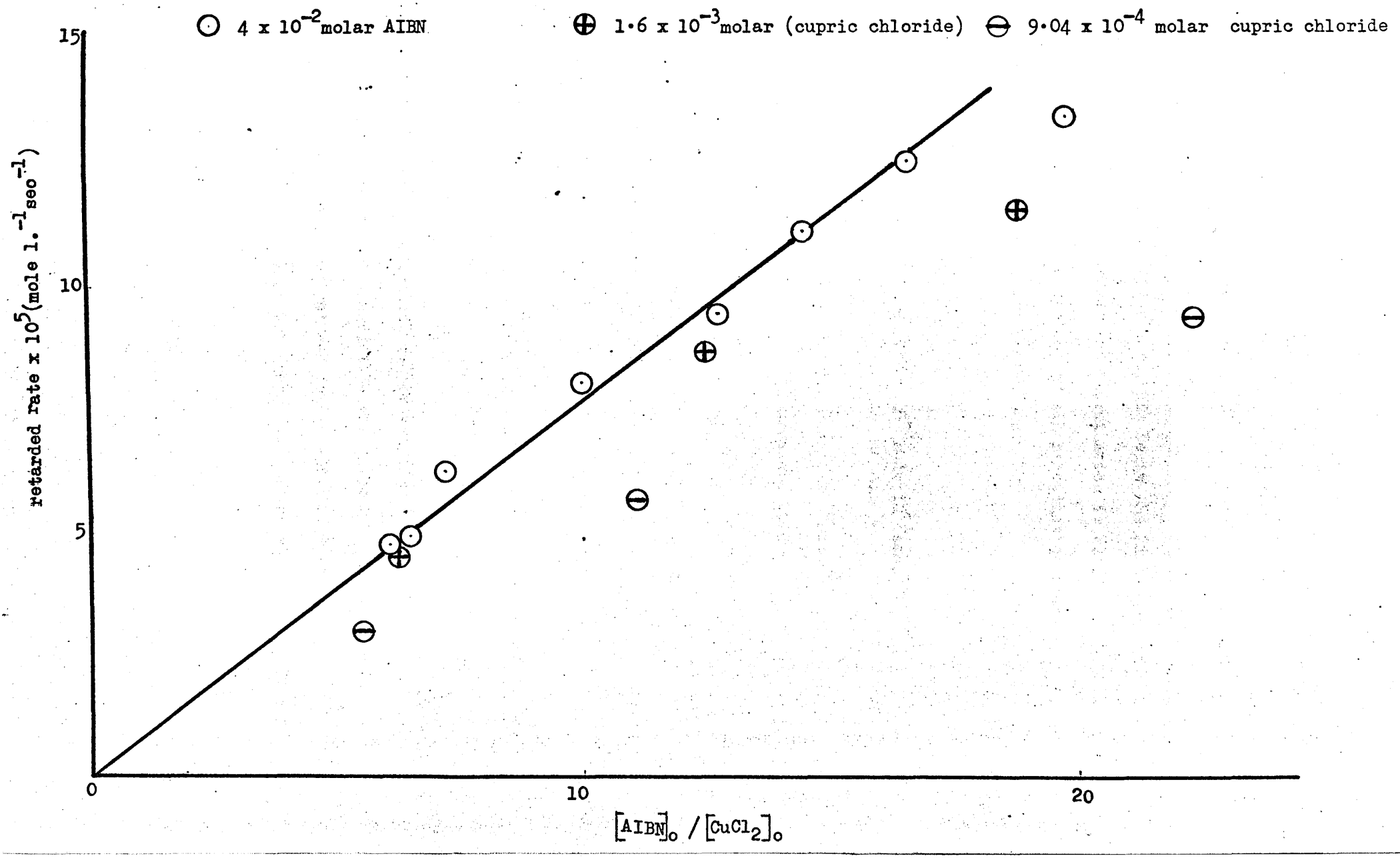
As described in the kinetic analysis (pages 24-30), the termination rate constants k_x and k_y for the reaction of polymer radicals with cupric and cuprous chloride respectively may be evaluated if the contribution of termination by mutual bi-radical reaction is considered negligible.

Fig. 5 shows the steady retarded rate after the inhibition period plotted against the ratio of initial AIBN to cupric chloride concentrations ($[AIBN]/[CuCl_2]_o$) for $[AIBN]$ varying from 5×10^{-3} to 4×10^{-2} mole $l.^{-1}$ and $[CuCl_2]_o$ from 9×10^{-4} to 6.5×10^{-3} mole $l.^{-1}$. If termination occurs exclusively by first order termination with respect to polymer radical concentration, the rate is determined by equation (38),

$$\text{Rate} = k_p I[M]/k_y[CuCl] \qquad (38)$$

and the plot should be a straight line of slope $k_p 2k_i[M]/k_y$. The plot given in fig. 5 shows that for the reaction initiated with 4×10^{-2} mole $l.^{-1}$ AIBN, those with cupric chloride concentrations greater than 2.4×10^{-3} mole $l.^{-1}$ lie on the

Fig.5. The effect of the initial cupric chloride and AIBN concentrations on the final retarded rate in the polymerisation of AN at 60°C.



straight line while at a lower initiator concentration (10^{-2}mole $l.^{-1}$) a slightly lower cupric chloride concentration ($1{\cdot}6 \times 10^{-3}$mole $l.^{-1}$) appears to fit the plot. The remainder of the experimental points clearly lie below the line indicating that some second order termination is also occurring, and these are typical of all reactions carried out at lower cupric chloride concentrations.

From fig. 5

$$\text{Slope} = k_p 2k_i[M]/k_y = 7{\cdot}7 \times 10^{-6} \text{mole } l.^{-1} \text{sec.}^{-1}$$

Using the average value of $1{\cdot}61 \times 10^{-5}$sec.$^{-1}$ for $2k_i$ obtained from inhibition measurements then

$$k_y/k_p = 6,$$

and correcting this for the slight loss of AIBN due to its decomposition during the inhibition period then

$$k_y/k_p = 5{\cdot}4$$

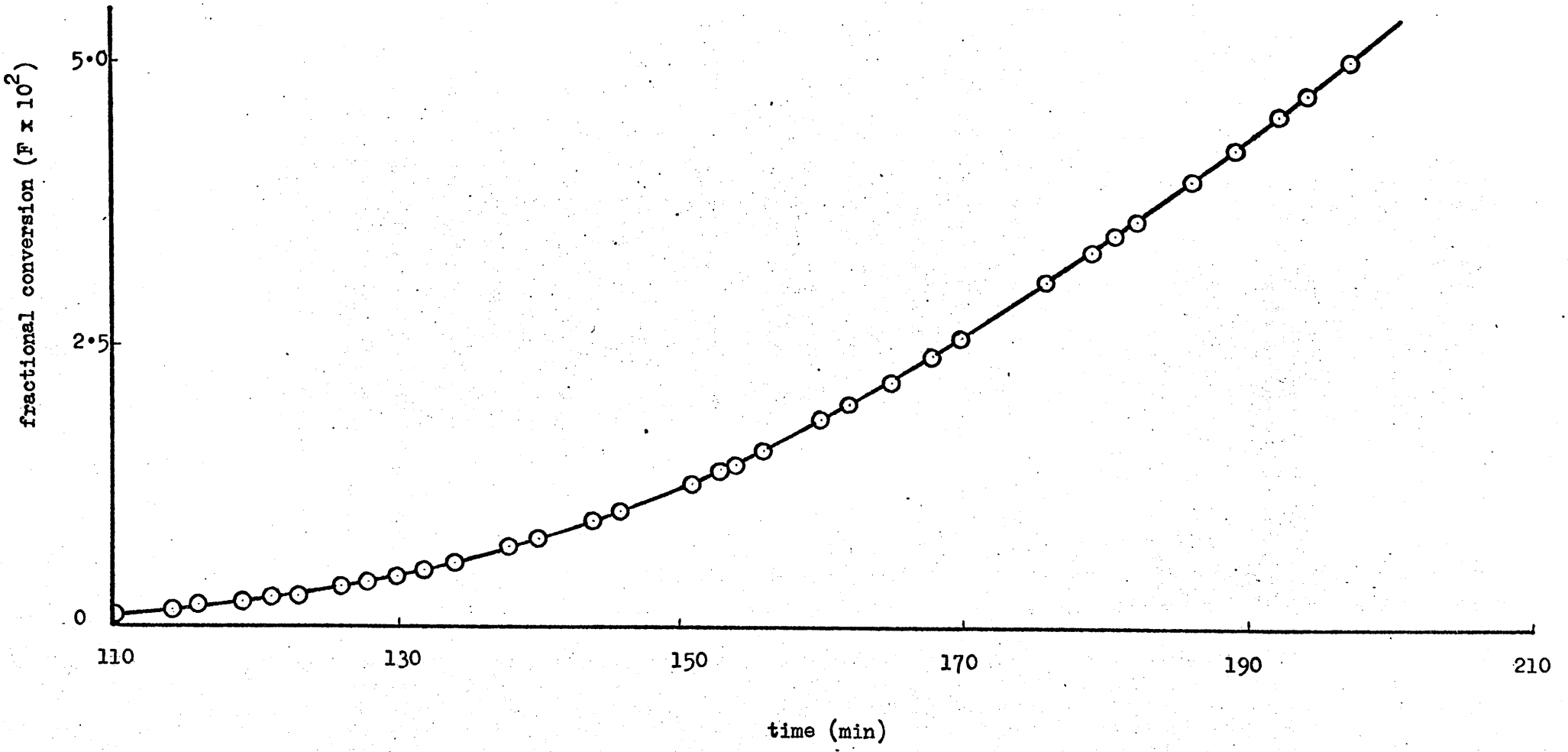
Using the value of 1930 l.mole^{-1}sec.$^{-1}$ for k_p at 60°C we obtain a value of $1{\cdot}04 \times 10^4$ l.mole^{-1}sec.$^{-1}$ for k_y at 60°C.

In the concentration region where mutual biradical termination is considered negligible the value of k_x, the rate constant for the reaction between polyacrylonitrile and cupric chloride, may be determined from the period of acceleration following complete inhibition.

Fig. 6 illustrates a typical conversion/time plot of the acceleration period following inhibition for the reaction initiated by $4{\cdot}0 \times 10^{-2}$mole $l.^{-1}$ AIBN in the presence of

Fig.6. Conversion against time for the acceleration period for the polymerisation of AN at 60°C.

$[CuCl_2]_o$ = $6{\cdot}13 \times 10^{-3}$ mole $l.^{-1}$ [AIBN] = $4{\cdot}0 \times 10^{-2}$ mole $l.^{-1}$



$6{\cdot}13 \times 10^{-3}$ mole $l.^{-1}$ $CuCl_2$. Measurements of the reduced rate, ϕ', are made by drawing tangents to the curve at known values of conversion.

The values of the reduced rate ϕ' are substituted in equation (46),

$$-\frac{1}{\phi'} - \ln\frac{(1-\phi')}{\phi'} = k_x[R]_y t + \text{constant} \qquad (46)$$

The plot of the left hand side of equation (46) against t should give a straight line of gradient $k_x[R]_y$. The value of the ratio k_x/k_p may then be obtained by substituting the various values in equation (54),

$$k_x/k_p = k_x[R]_y[M]/(-d[M]/dt)_y \qquad (54)$$

Alternatively k_x/k_p may be obtained from equation (57),

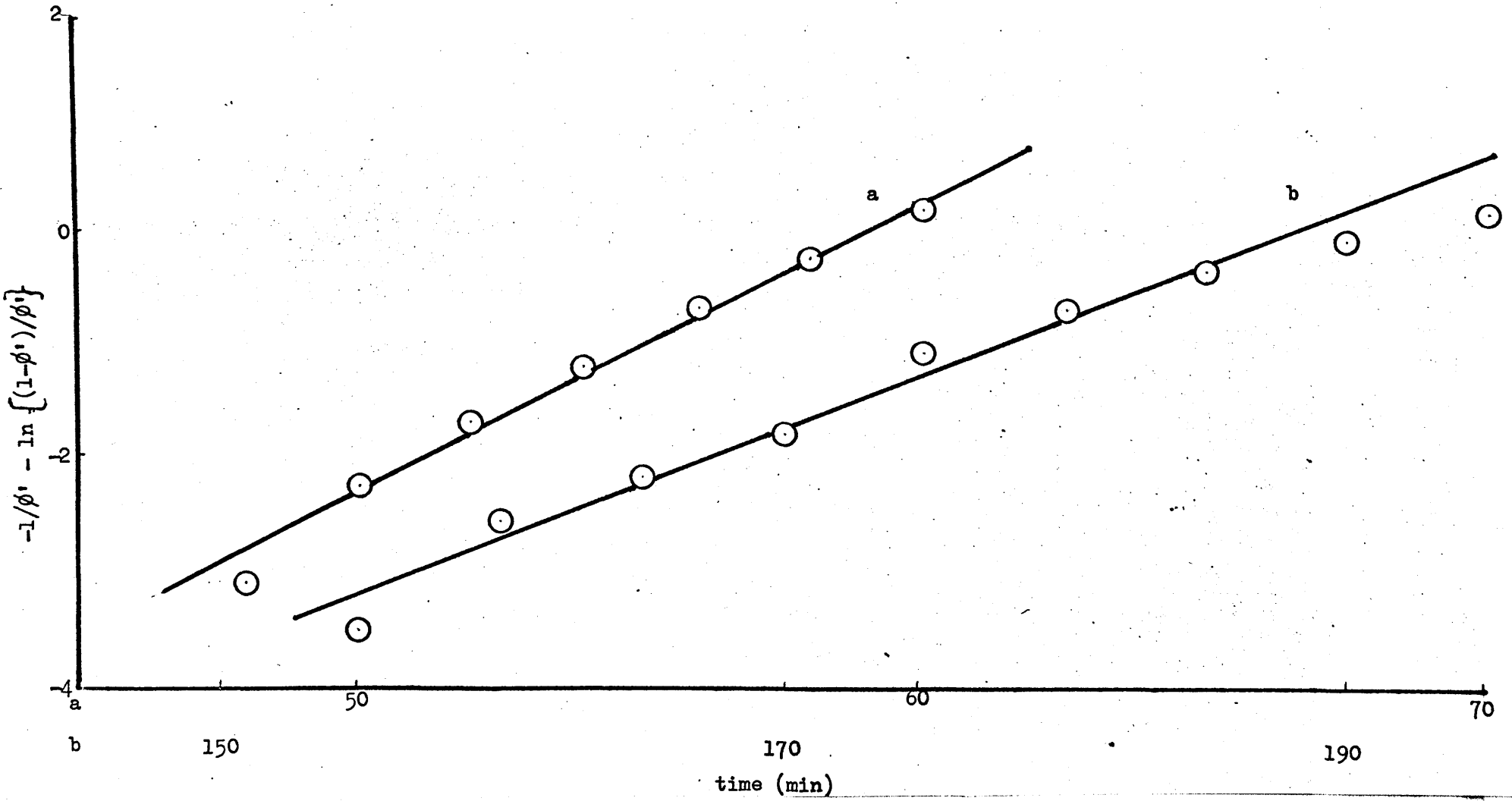
$$\left\{(k_x/k_y)-1\right\} = \left\{(1/\phi')-1\right\}/(1-F)^{k_x/k_p} \qquad (57)$$

The plot of $\log\left\{(1/\phi')-1\right\}$ against (1-F) should be a straight line of slope k_x/k_p.

The plot of the left hand side of equation (46) against time is given in fig. 7 for polymerisations carried out in the presence of $2{\cdot}02$ and $6{\cdot}55 \times 10^{-3}$ mole $l.^{-1}$ cupric chloride and initiated with 4×10^{-2} mole $l.^{-1}$ AIBN. The calculation of the functions from the dilatometric measurements is shown in the Appendix. The ϕ' values used in these calculations were restricted to the range $0{\cdot}4 < \phi' < 0{\cdot}8$ because the dependence of the function $-1/\phi' - \ln\left\{(1-\phi')/\phi'\right\}$ on ϕ' is minimal

Fig.7. l.h.s. of equation (46) against time for the polymerisation of AN initiated with 4×10^{-2} molar AIBN.

(a) $[CuCl_2]_o = 2{\cdot}02 \times 10^{-3}$ mole $l.^{-1}$ (b) $[CuCl_2]_o = 6{\cdot}55 \times 10^{-3}$ mole $l.^{-1}$



within this range as illustrated in fig. 8 and also because of the increased error associated with the assignment of exact F values to ϕ' measurements at values of ϕ' less than 0·2 or greater than 0·8. The plots shown in fig. 7 are reasonably linear, as were the plots obtained for intermediate cupric chloride concentrations. The slopes for curves 'a' and 'b' are 0·094 min^{-1} and 0·262 min^{-1} respectively, which substituted in equation (54) give values of k_x/k_p of 93·6 and 96·5 respectively. The values of k_x/k_p calculated in this way are shown in column 3 of Table 4.

Fig. 9 shows the plot of $\log\left\{(1/\phi')-1\right\}$ against $\log(1-F)$ using the same measured values of ϕ' and F that were used in fig. 7. The plots are again reasonably linear and in this case ϕ' values in the range $0{\cdot}25<\phi'<0{\cdot}75$ were used, this being the region of minimum dependence of the function $\log\left\{(1/\phi')-1\right\}$ on ϕ', as illustrated in fig. 10. The values of k_x/k_p as measured from the slopes of the lines are shown in Table 4 with the values obtained at intermediate cupric chloride concentrations.

Table 4 /-

Fig. 8. Variation of $-1/\phi' - \ln\{(1-\phi')/\phi'\}$ with ϕ'.

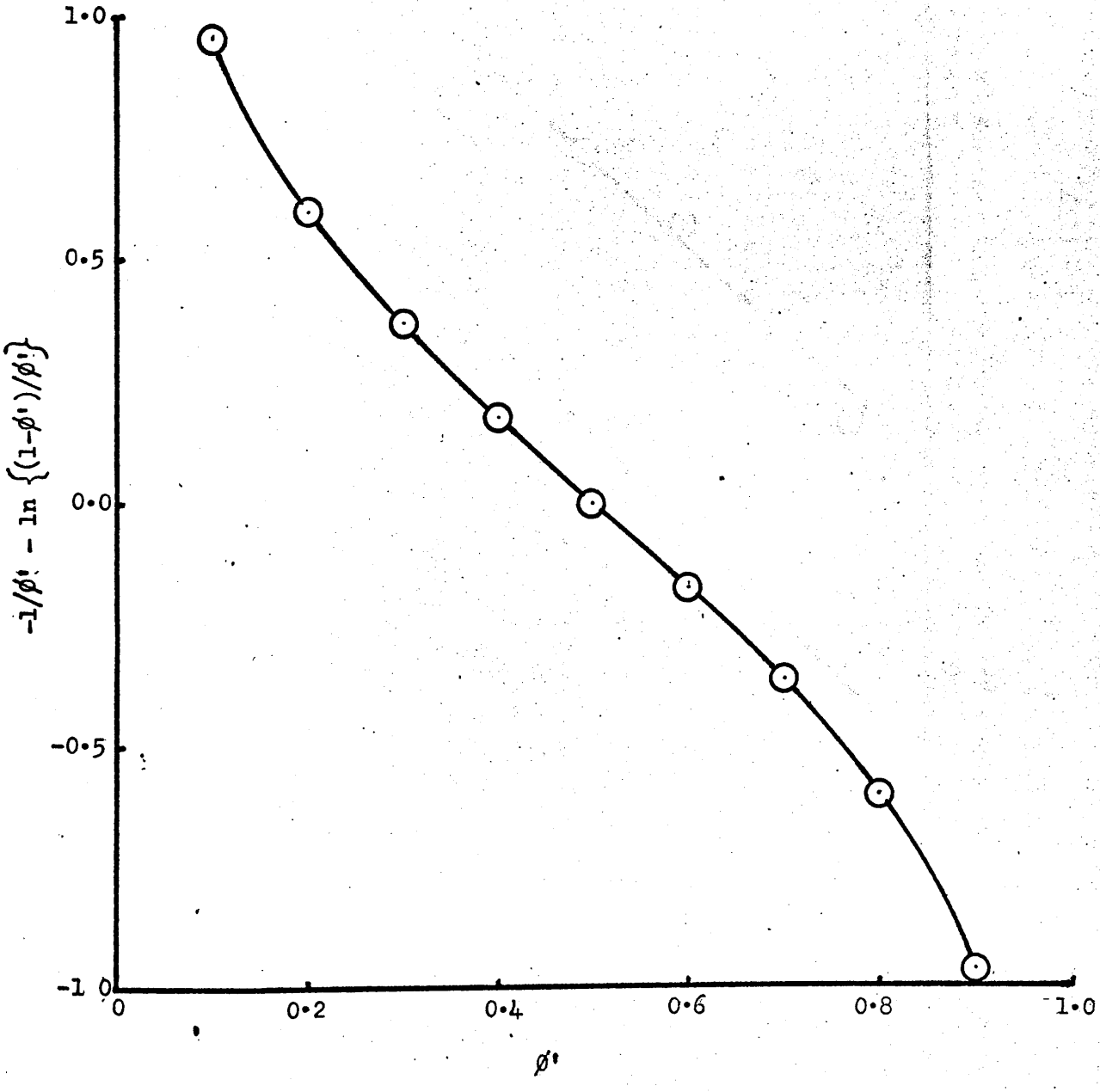


Fig.9. $\log\{(1/\phi')-1\}$ against log (1-F) for the polymerisation of AN initiated with 4×10^{-2} molar AIBN

(a) $[CuCl_2]_o = 2{\cdot}02 \times 10^{-3}$ mole $l.^{-1}$ (b) $[CuCl_2]_o = 6{\cdot}55 \times 10^{-3}$ mole $l.^{-1}$

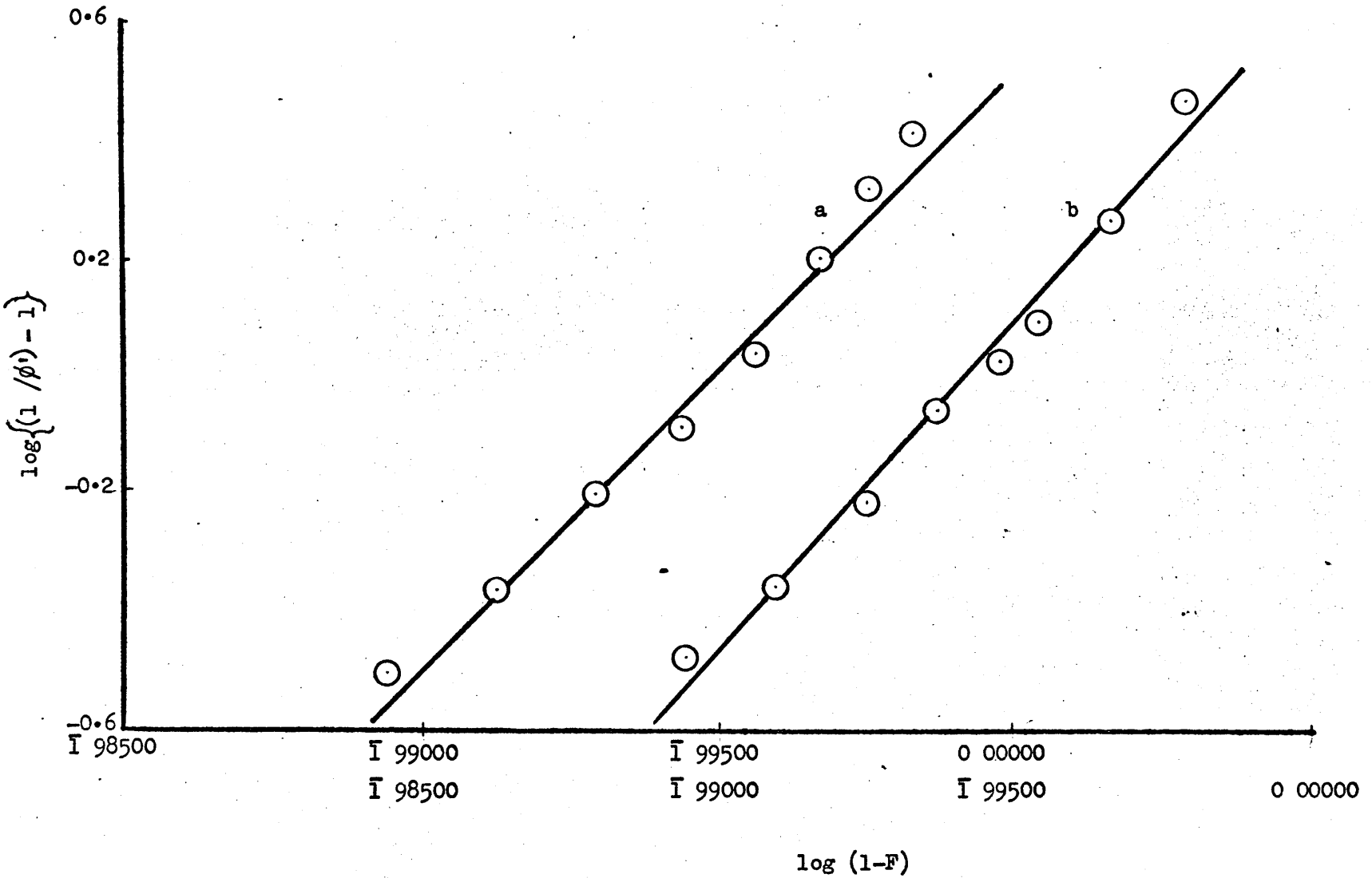


Fig. 10. Variation of $\log\{(1/\phi') - 1\}$

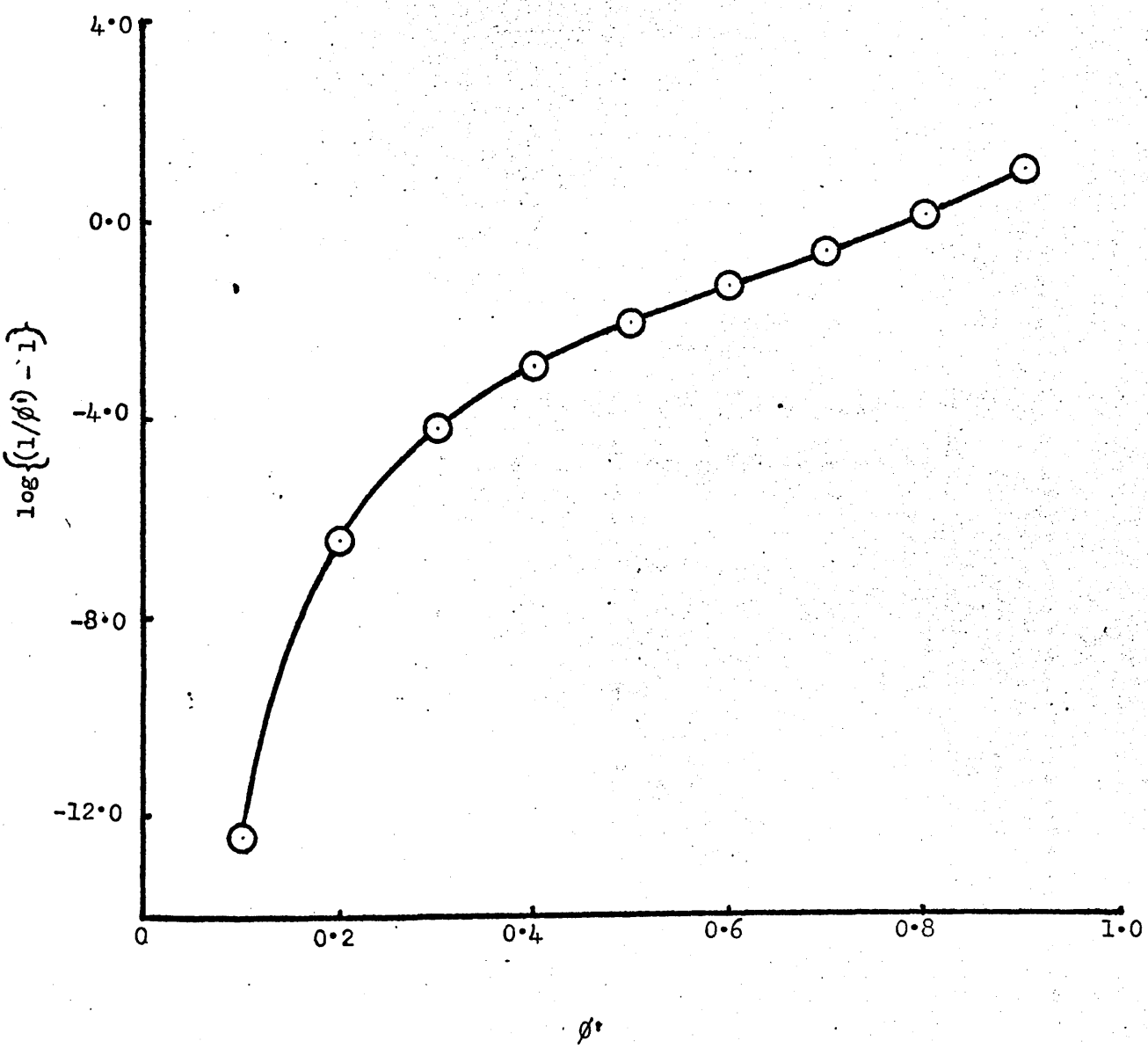


Table 4 - Values of k_x/k_p determined using equations (46) and (57) with results from the polymerisation of AN initiated by AIBN in the presence of $CuCl_2$ at 60°C.

$[CuCl_2]_o$	[AIBN]	values of k_x/k_p	
mole $l.^{-1}$ (x 10^3)	mole $l.^{-1}$ (x 10^2)	using eq.(46)	using eq.(57)
2·02		93·6	103
2·40	4·0	75·3	89·8
2·75		74·5	95·8
3·11		71·9	103
3·97		57·6	101
5·53		71·2	89
6·13		98·4	108
6·55		96·5	112

These give an average value of 100 for k_x/k_p (using equation 57). Using the value of 1930 $l.mole^{-1}sec^{-1}$ for k_p for AN at 60°C, k_x becomes $1·93 \times 10^{-5}$ $l.mole^{-1}sec^{-1}$.

Corrected Rate Constants.

As described by equation (53)

$$\text{Intercept} = \left\{1 - (k_y/k_x)\right\}[CuCl_2]_o/I \qquad (53)$$

the values for the rates of initiation calculated from the intercept of the extrapolated retarded rate of polymerisation to the time axis should be corrected by multiplying by the factor $\left\{1 - (k_y/k_x)\right\}$. Using the values of k_y and k_x already

given, the ratio k_y/k_x has a value of 0·054, and the rate of initiation correction factor becomes 0·946.

$\therefore$ The rate constant of initiation $= 1{\cdot}61 \times 10^{-5} \times 0{\cdot}946 \text{ sec}^{-1}$

$= 1{\cdot}52 \times 10^{-5} \text{sec}^{-1}$

Using this new value of $2k_i$, substituted in equation (38, k_y/k_p becomes 5·7 which gives a new value of k_y/k_x of 0·057; this in turn gives a new value of 1·515 sec^{-1} for $2k_i$. Successive approximations become smaller and smaller and can clearly be ignored. Thus the values obtained for the rate constants are

$$2k_i = 1{\cdot}51 \times 10^{-5} \text{sec}^{-1} ;$$

$$k_y = 1{\cdot}1 \times 10^{4} \text{l.mole}^{-1}\text{sec}^{-1} ;$$

$$k_x = 1{\cdot}93 \times 10^{5} \text{l.mole}^{-1}\text{sec}^{-1}.$$

In the derivation of these constants it has been assumed that the product ($CuClR_n$) of the reaction between the growing polyacrylonitrile radicals and the cuprous chloride (formed by the reaction between cupric chloride and polyacrylonitrile radicals) does not react with the growing polymer radicals. Such an assumption is not unreasonable since

(1) the final colour of the solution is fairly intense indicating that eventually a fairly high concentration of $CuClR_n$ is produced and

(2) it is known that the reactivity of cupric salts depends largely upon the ligands present (see later sections).

If, however, the product $CuClR_n$ does react with the

polyacrylonitrile radicals then the post inhibition steady rate will be attained only when the ratio of CuCl to $CuClR_n$ becomes constant. This would occur when the rates of reactions (36a.) and (36b.) become equal.

$$R_n + CuCl \xrightarrow{k_y} CuClR_n \qquad (36a.)$$

$$R_m + CuClR_n \xrightarrow{k_z} CuCl + \text{polymer} \qquad (36b.)$$

$$\text{i.e.} \quad k_z[R][CuClR_n] = k_y[R][CuCl] \qquad (58)$$

Thus at the end of the inhibition period when all the cupric chloride has reacted we have

$$[CuCl] + [CuClR_n] = [CuCl_2]_o \qquad (59)$$

From (58) and (59) we have

$$[CuCl] = [CuCl_2]_o / (1 + k_y/k_z) \qquad (60)$$

Equation (45) will be replaced by the following equation

$$[R]_y = I/(k_y[CuCl] + k_z[CuClR_n]) \qquad (61)$$

Combining equations (58), (60) and (61) we have

$$[R]_y = I(1 + k_y/k_z)/2k_y[CuCl_2]_o \qquad (62)$$

Consider, firstly, the unlikely event of the product $CuClR_n$ being very reactive, i.e. $k_z \gg k_y$, then equation (62) approximates to

$$[R]_y = \frac{I}{2k_y[CuCl_2]_o} \qquad (63)$$

i.e. the value of k_y determined by equation (45) will be out by a factor of 2.

Secondly, if we assume that $CuClR_n$ and CuCl are equally reactive towards polyacrylonitrile radicals, i.e. $k_y = k_z$, then equation (62) reverts to equation (45) and no correction to the k_y value is necessary.

SECTION 2 - THE POLYMERISATION OF METHYL METHACRYLATE IN THE PRESENCE OF SOME CUPRIC SALTS

CONVERSION FACTOR

For the polymerisation of methyl methacrylate, a linear relationship between fractional contraction, V/Vo, and fractional conversion, F, was found to hold over the first 10% polymerisation.

For methyl methacrylate at 60°C

$$V/Vo = 0{\cdot}234 \times F$$

This is in good agreement with the conversion factor (0·237) calculated from the density data of Matheson et al.[41].

For polymerisation studies of methyl methacrylate at temperatures other then 60°C, conversion factors are calculated from the densities of monomer and polymer at the required temperature. The values obtained from these are as follows.

Temperature (°C)	V/Vo / F
40	0·221
50	0·228
70	0·243

THE POLYMERISATION OF METHYL METHACRYLATE IN THE PRESENCE OF CUPRIC CHLORIDE

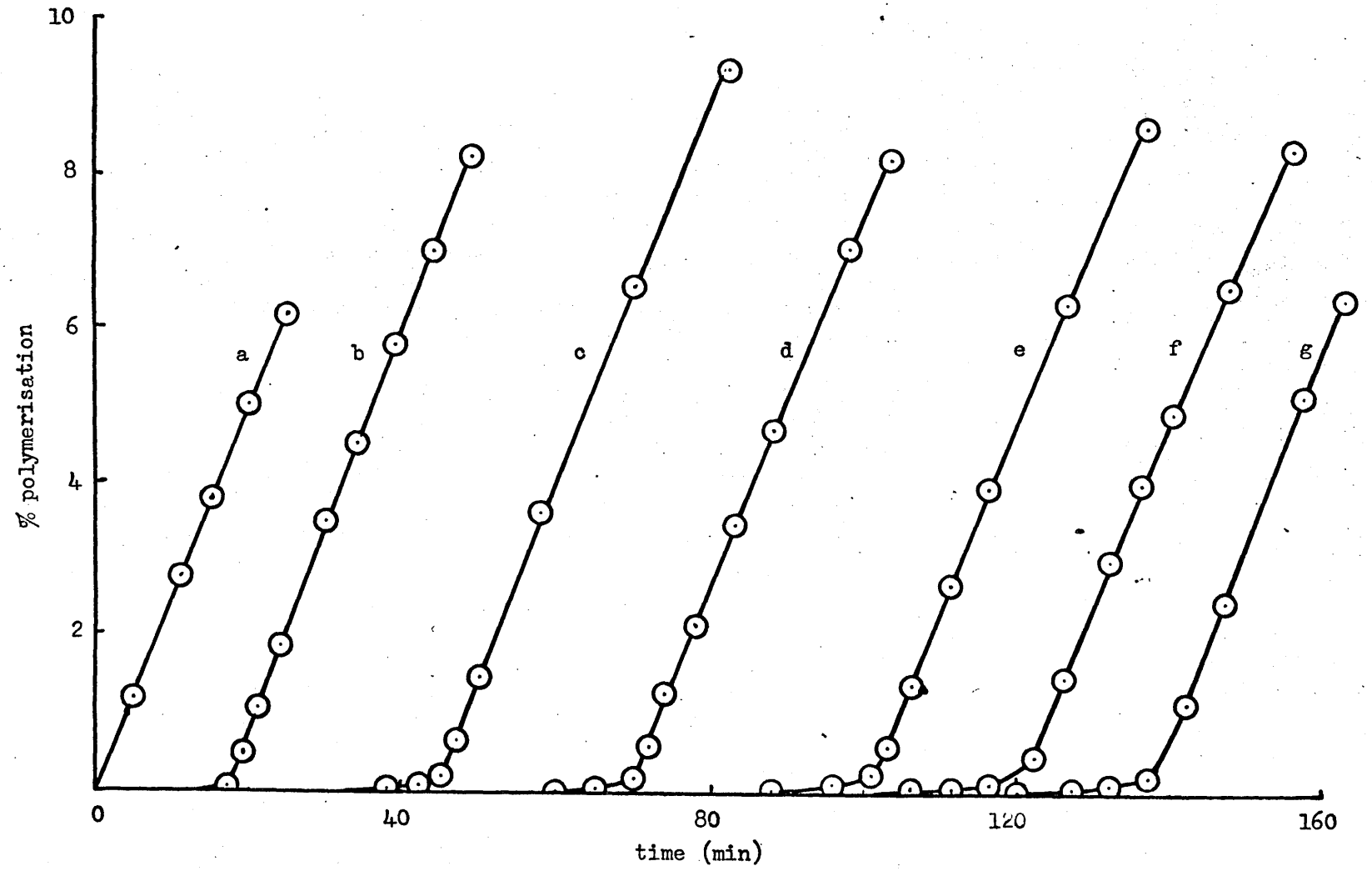
The initial experiments were all carried out at 60°C, with the volume ratio of MM/DMF being kept constant at 90%/10% such that $[M] = 8{\cdot}06$ mole $l.^{-1}$. The small quantity of solvent is required as cupric chloride is almost completely insoluble in MM.

The effect of cupric chloride on the polymerisation of methyl methacrylate initiated with $1{\cdot}08 \times 10^{-2}$ mole $l.^{-1}$ AIBN was first studied. As with acrylonitrile, the polymerisation is inhibited, the inhibition period increasing with increasing initial cupric chloride concentration. The final rate of polymerisation is not affected by the addition of cupric chloride, so the probable product of the reaction, cuprous chloride, does not appear to affect the polymerisation. The period of inhibition is followed by a rapid acceleration in rate until the final steady rate is attained. A substantial $[AIBN]/[CuCl_2]_o$ ratio was maintained throughout the experiments to avoid errors in the final rate of polymerisation due to AIBN decomposition during the inhibition period. Fig.11 refers to polymerisation against time curves for initial concentration of cupric chloride up to $1{\cdot}3 \times 10^{-3}$ mole $l.^{-1}$. During the inhibition period the cupric chloride colour faded gradually and disappeared completely by the end of the inhibition. In contrast to the results with acrylonitrile, the solution remained colourless during polymerisation.

Fig.11 The effect of cupric chloride on the polymerisation of methyl methacrylate.

$[AIBN] = 1{\cdot}08 \times 10^{-2}$ mole $l.^{-1}$.

$[CuCl_2] = 0, 1{\cdot}71, 4{\cdot}35, 6{\cdot}25, 8{\cdot}02, 10{\cdot}43$ and $13{\cdot}04 \times 10^{-4}$ mole $l.^{-1}$ for curves a - g respectively.

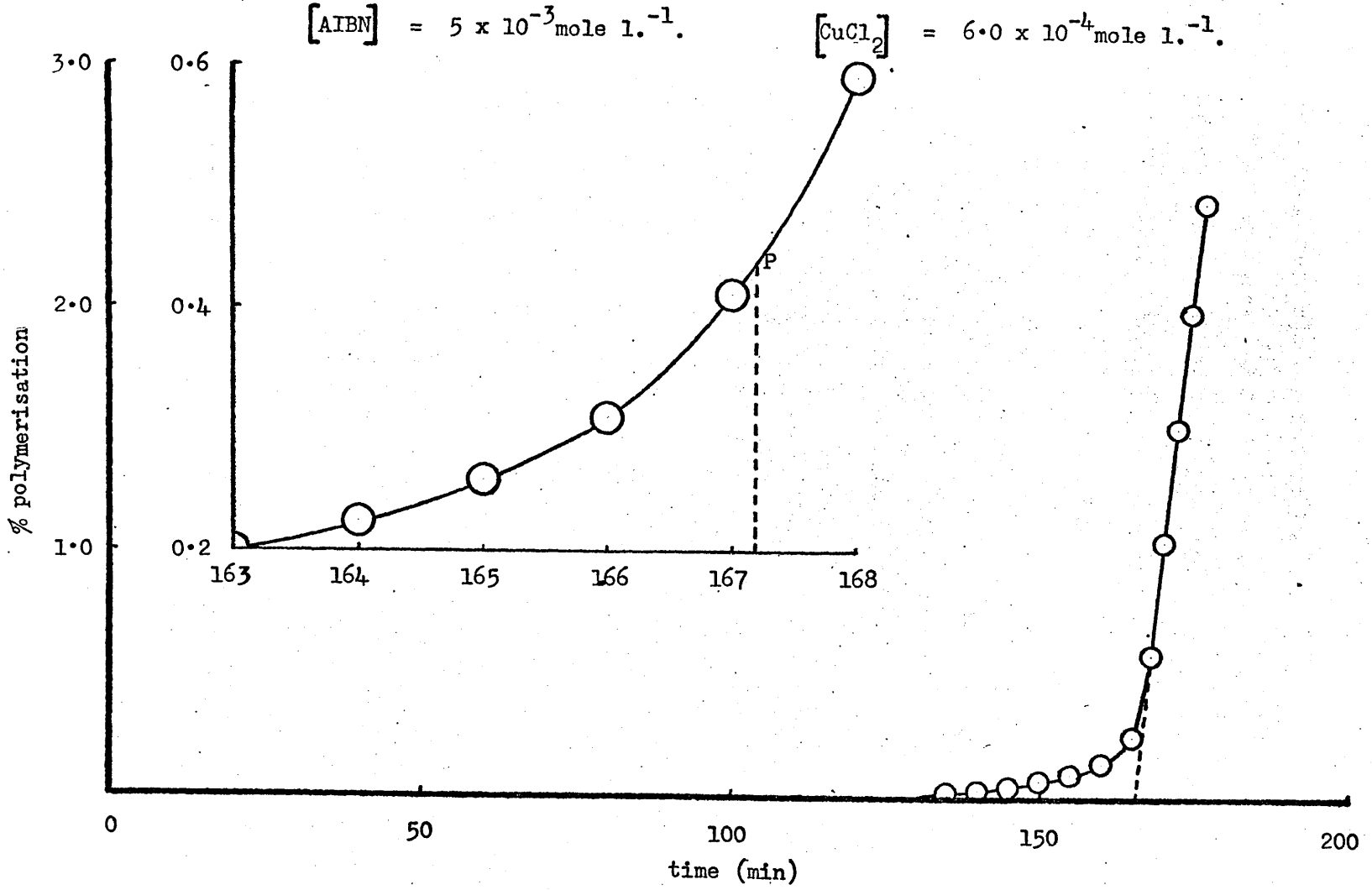


MEASUREMENT OF INHIBITION PERIODS.

For the conditions existing in this reaction, Bamford et al.[2] have shown that the time t', at which the value of ϕ_t, the reduced rate, = 0·648, is a more satisfactory measure of the induction period than the usual extrapolation of the % polymerisation against time curve to the time axis.

A typical example of the % polymerisation against time curves obtained with methyl methacrylate in the presence of cupric chloride is given in fig. 12. The insert shows a detailed plot of part of the acceleration period, with P indicating the point at which ϕ_t = 0·648. This gives a value of 167·2 min. for t'. The extrapolation of the linear portion of the % polymerisation against time curve gives an inhibition period of 165·6 min., i.e. slightly less than t' as expected from theory [2]. The difference in the two values is, however, only about 1% of the inhibition period. Consequently, if the extrapolation method were used it would result in the value of the rate of initiation being too large by about 1%. As errors in reproducibility are normally greater than 1%, then if a measure of the rate of initiation only is required, it is simpler to adopt the usual extrapolation procedure, since to determine t' accurately it is necessary to make a detailed study of the period of acceleration using large dilatometers with small capillaries. Since the usual extrapolation technique is, however, accurate even when relatively small dilatometers are used, it has been applied to the determinations involving measurement of rates of initiation.

Fig.12 The polymerisation of methyl methacrylate inhibited by cupric chloride.
Insert shows part of acceleration period.



EVALUATION OF RATES OF INITIATION.

The inhibition periods measured from the polymerisation curves, shown in fig. 11 were plotted against the initial cupric chloride concentrations. The plot gives a straight line passing through the origin, showing no inhibition in the absence of cupric chloride. This plot is shown in fig. 13 together with similar plots at AIBN concentrations of $2{\cdot}05 \times 10^{-2}$ mole $l.^{-1}$ and $5{\cdot}0 \times 10^{-3}$ mole $l.^{-1}$. The slopes of these lines gives the rates of removal of cupric chloride from the monomer and assuming that each free radical reacts with one molecule of cupric chloride, then the rate of removal of cupric chloride is equal to the rate of initiation, I.

The plot of I against the AIBN concentration is given in fig. 14. It is linear and can be represented by

$$I = 1{\cdot}38 \times 10^{-5}[\text{AIBN}] \quad (\text{mole } l.^{-1} \text{sec}^{-1})$$

Fig. 15 refers to a plot of the rate of polymerisation against the square root of the AIBN concentration. The plot is linear and passes through the origin, showing that once the inhibitor had been removed the termination process again became second-order with respect to the growing polymer radicals.

THE POLYMERISATION OF METHYL METHACRYLATE IN THE PRESENCE OF CUPRIC BROMIDE

As with the reaction involving cupric chloride, the initial measurements were carried out at 60°C with $[M] = 8{\cdot}06$ mole $l.^{-1}$.

Fig.13 The effect of cupric chloride on the inhibition period for the polymerisation of methyl methacrylate.

$[AIBN] = 2{\cdot}05 \times 10^{-2}$, $1{\cdot}08 \times 10^{-2}$ and $5{\cdot}0 \times 10^{-3}$ mole $l.^{-1}$ for curves a, b and c respectively.

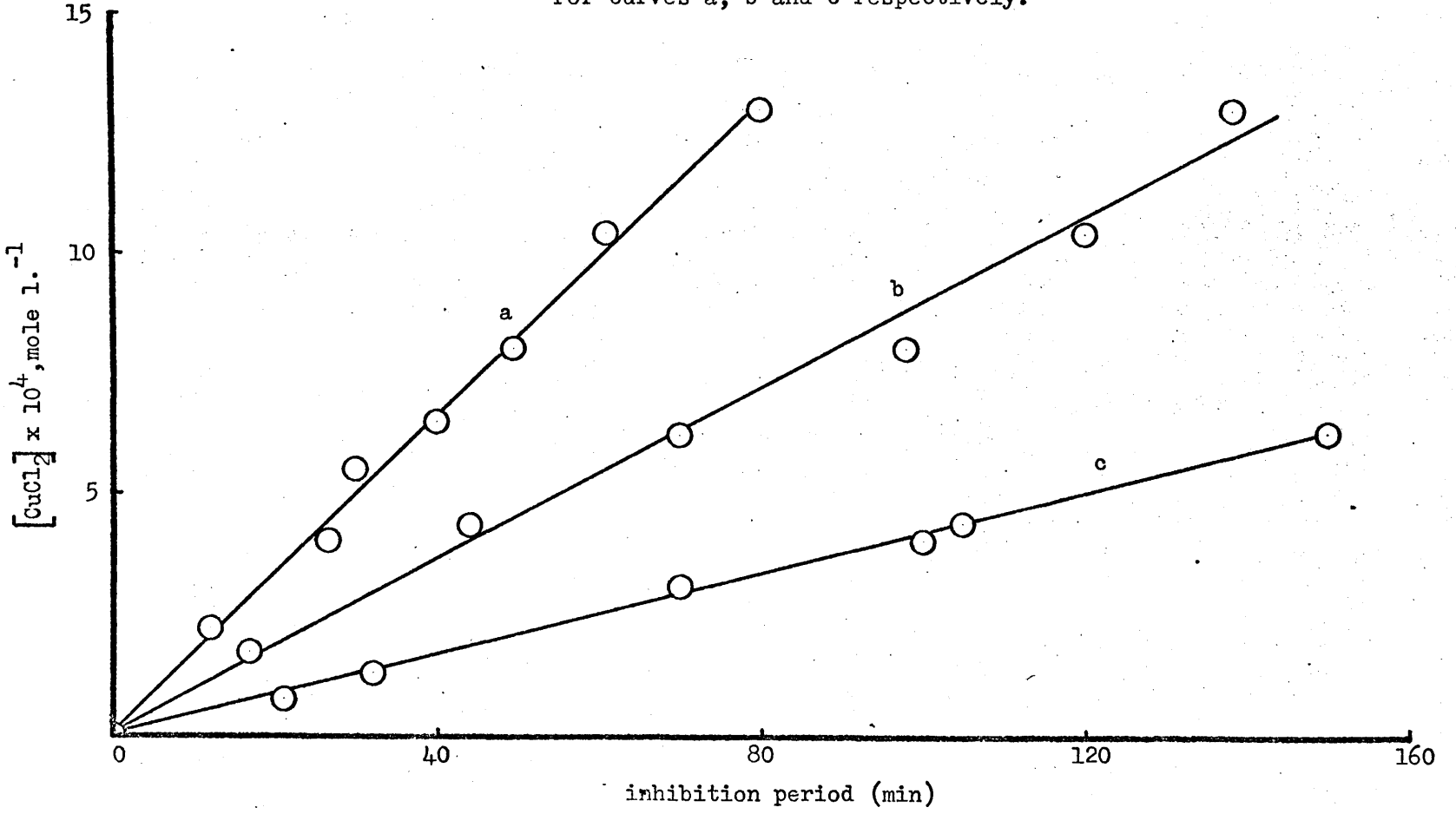


Fig.14 The effect of AIBN concentration on the rate of initiation of the polymerisation of methyl methacrylate.

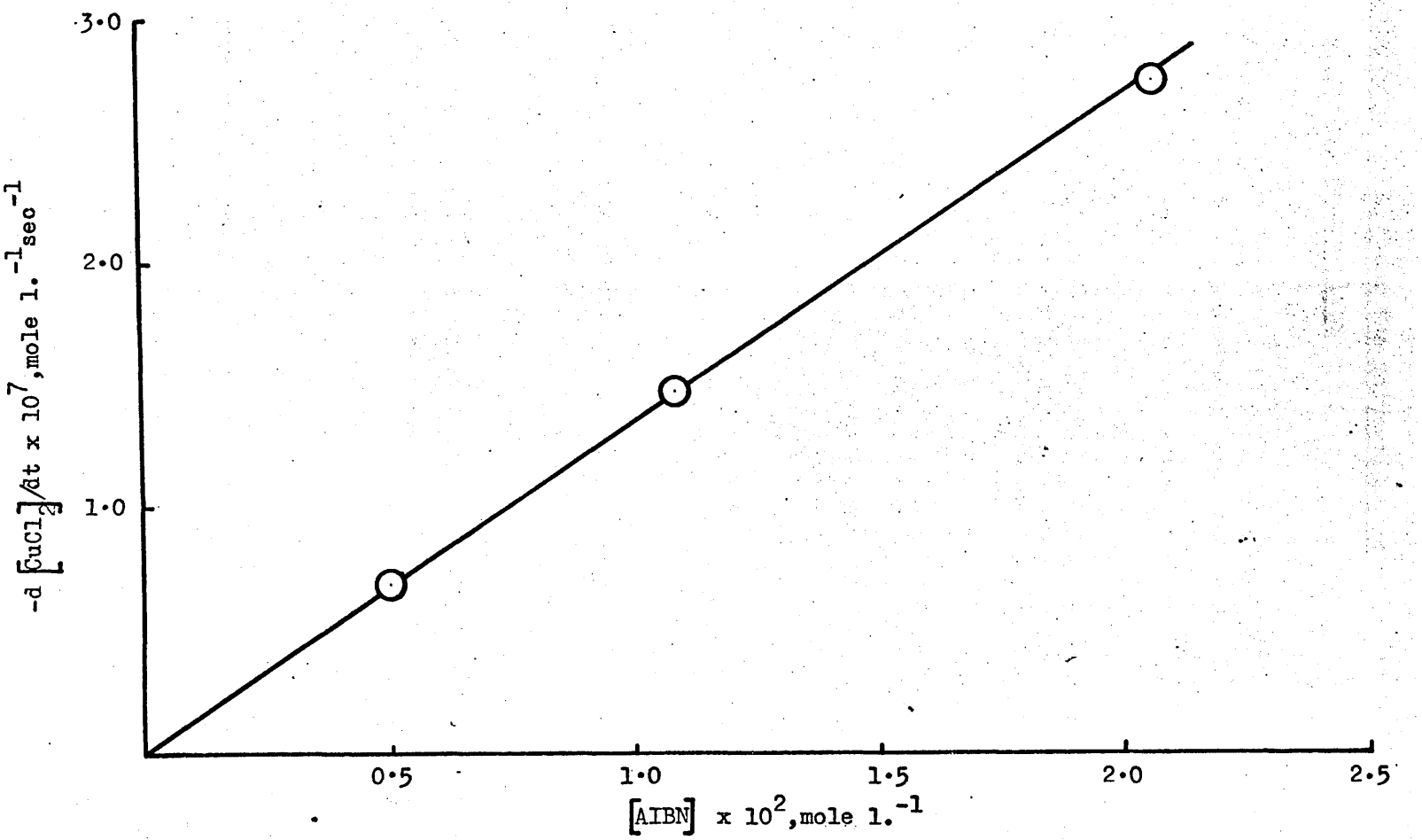
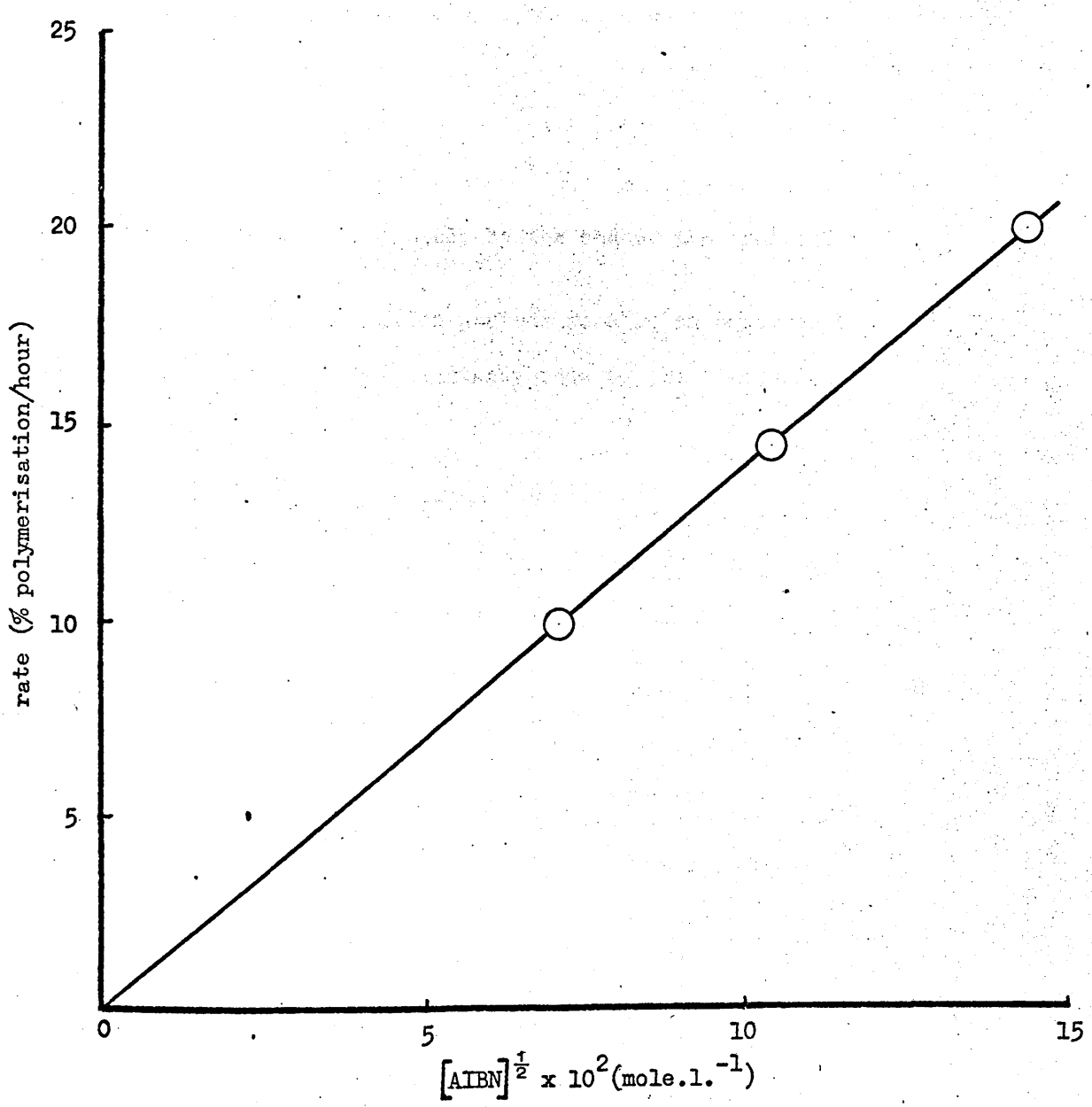


Fig.15 Rate dependence on $[AIBN]^{\frac{1}{2}}$ for the polymerisation of methyl methacrylate



The polymerisation was first studied at an AIBN concentration of 1×10^{-2} mole $l.^{-1}$ in the presence of cupric bromide concentrations up to $1{\cdot}13 \times 10^{-3}$ mole $l.^{-1}$. Fig. 16 shows the % polymerisation against time curves. As with cupric chloride, the polymerisation is inhibited, the inhibition period being followed by a rapid acceleration in rate to the value obtained in the absence of inhibitor. Thus is appears that cuprous bromide, the probable product of the inhibition reaction, has no affect on the polymerisation. The cupric bromide colour faded during the inhibition period and disappeared completely by the end of the inhibition.

The inhibition periods were again measured by extrapolating the final steady rate to the time axis.

EVALUATION OF RATES OF INITIATION

Fig. 17 shows inhibition periods plotted against initial cupric bromide concentrations for an AIBN concentration of 1×10^{-2} mole $l.^{-1}$. The plot is linear and passes through the origin, giving the rate of removal of cupric bromide as

$$-\frac{d[CuBr_2]}{dt} = 1{\cdot}4 \times 10^{-7} \text{ mole } l.^{-1} \text{sec}^{-1}.$$

Again assuming that each free radical reacts with one molecule of cupric salt, then

$$-\frac{d[CuBr_2]}{dt} = I = 1{\cdot}4 \times 10^{-5}[AIBN] \quad (\text{mole } l.^{-1} \text{sec}^{-1})$$

Fig.16 The effect of cupric bromide on the polymerisation of methyl methacrylate.

$[AIBN] = 1 \times 10^{-2}$ mole $l.^{-1}$. $[CuBr_2] \times 10^4$ mole $l.^{-1}$.

0	for curve a
2·77	b
4·97	c
7·0	d
9·13	e
11·3	f

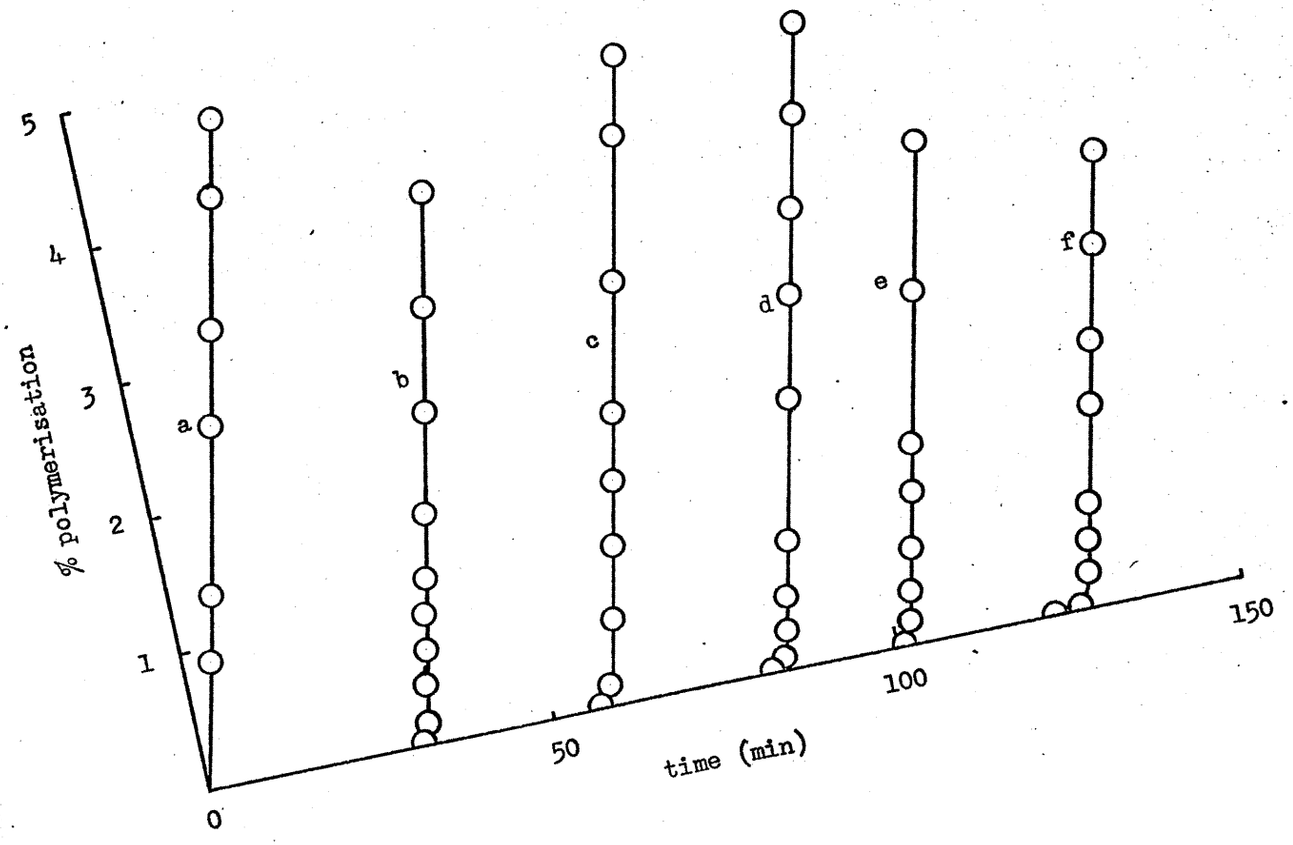
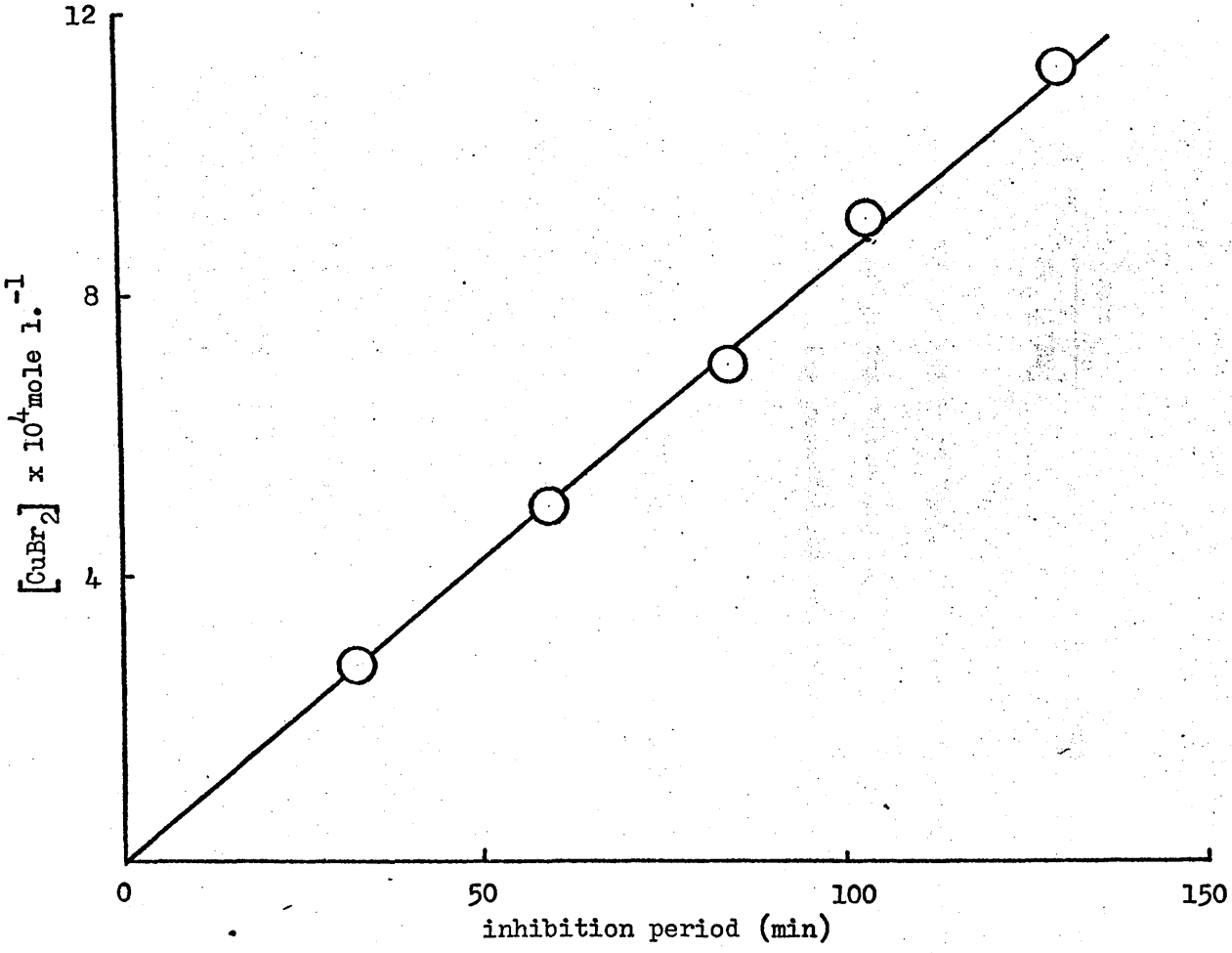


Fig.17 The effect of cupric bromide on the inhibition period for the polymerisation of methyl methacrylate.

$[AIBN] = 1 \times 10^{-2}$ mole $l.^{-1}$.



A series of polymerisations were studied at constant initial cupric bromide concentrations and varying AIBN concentrations. Fig. 18 shows that the length of the inhibition period, T, is inversely proportional to the catalyst concentration for a given initial cupric bromide concentration. With the assumption that each free radical reacts with one molecule of cupric bromide then

$$T = \frac{[CuBr_2]_o}{2k_i [AIBN]} \qquad (36)$$

The slope of the line in fig. 18 is $1{\cdot}98 \times 10^{-2}$ mole $l.^{-1}$ sec. which when substituted in equation (36), gives the value for $2k_i = 1{\cdot}39 \times 10^{-5} sec^{-1}$, in conformity with the result obtained from fig. 17.

Fig. 19 illustrates that once the inhibitor had been removed the termination again became second-order with respect to the growing polymer radicals.

EFFICIENCY OF INITIATION.

Using the value of $1{\cdot}01 \times 10^{-5} sec^{-1}$ for k_d at 60°C, the efficiency of initiation is approximately 70% with both cupric chloride and cupric bromide.

Fig.18 Dependence of induction period T on the AIBN concentration.

$[CuBr_2] = 7 \times 10^{-4}$ mole $l.^{-1}$.

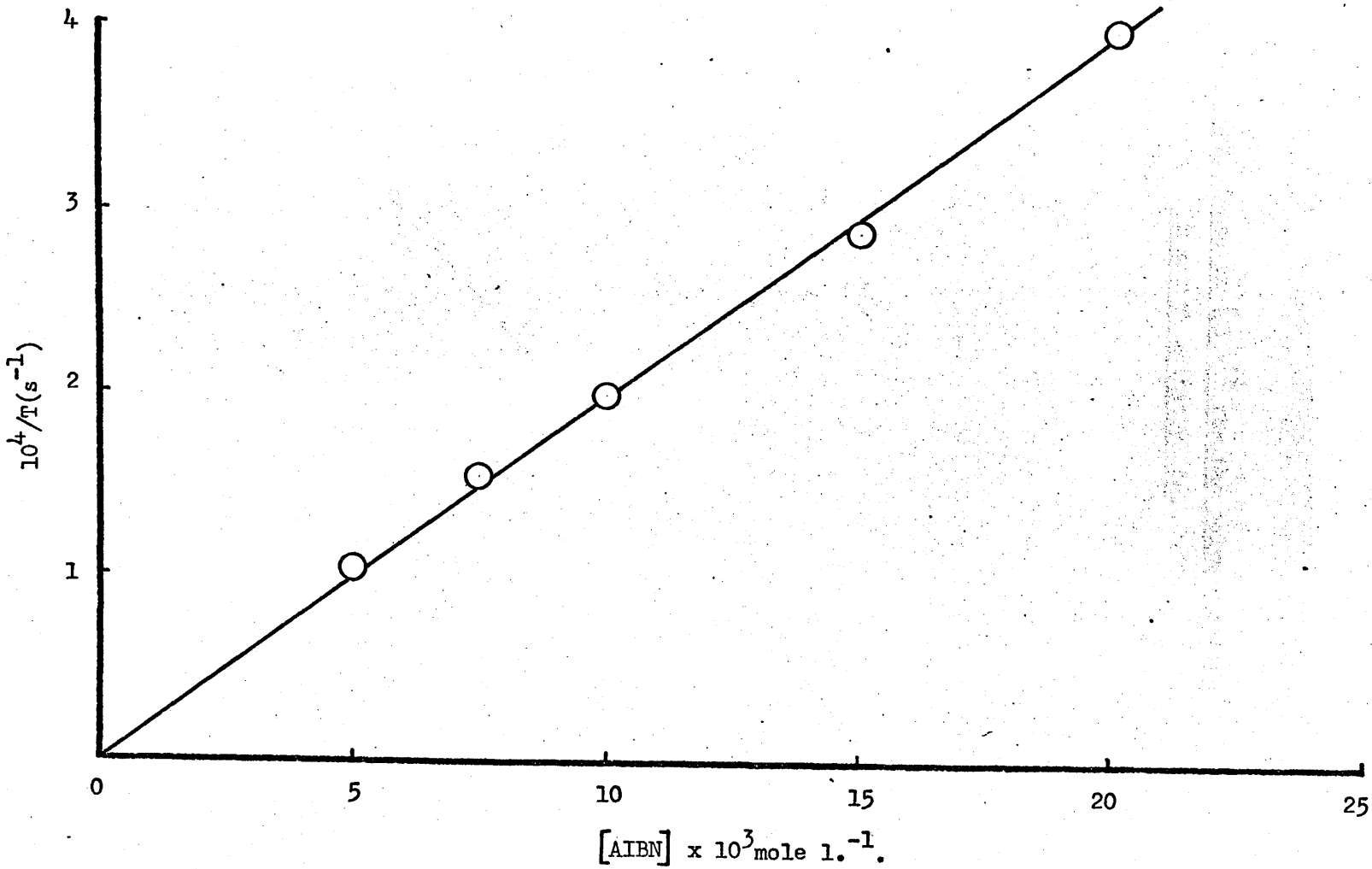
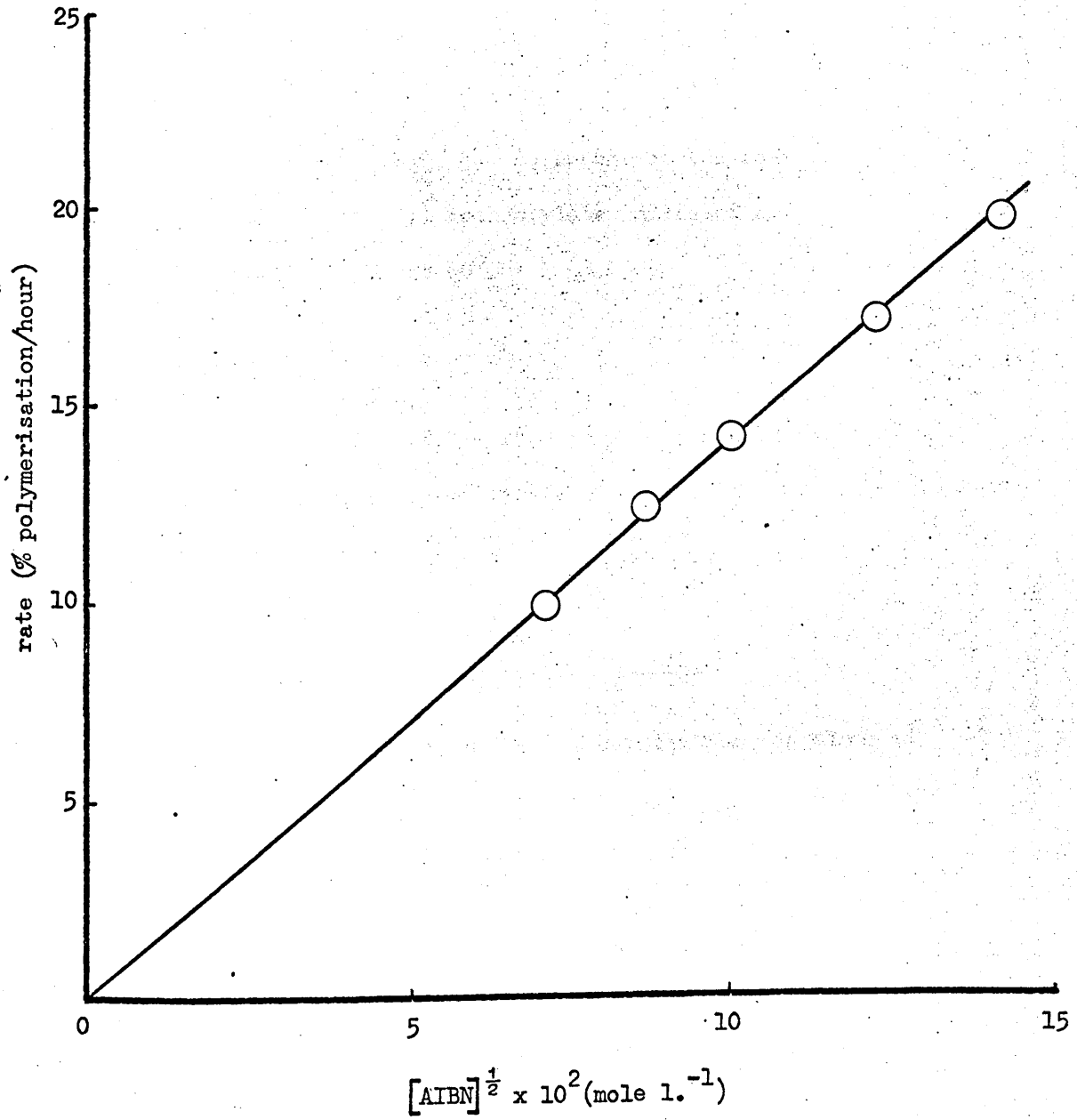


Fig.19 Rate dependence on $[AIBN]^{\frac{1}{2}}$ for the polymerisation of methyl methacrylate.



THE POLYMERISATION OF METHYL METHACRYLATE IN THE PRESENCE OF CUPRIC NITRATE AND CUPRIC ACETATE

In these experiments, it was essential to use DMF as solvent due to the insolubility of the salts in methyl methacrylate. The monomer concentration in each case was 8·06 mole $l.^{-1}$

CUPRIC ACETATE.

The presence of 1·3 and 5·4 x 10^{-3} mole $l.^{-1}$ cupric acetate, $Cu(CH_3COO)_2.H_2O$, had no effect on the rate of polymerisation of methyl methacrylate initiated by 1 x 10^{-2} mole $l.^{-1}$ AIBN at 60°C.

CUPRIC NITRATE.

The presence of 1·9 and 9·8 x 10^{-3} mole $l.^{-1}$ cupric nitrate, $Cu(NO_3)_2.3H_2O$, had no effect on the rate of polymerisation of methyl methacrylate initiated by 1 x 10^{-2} mole $l.^{-1}$ AIBN at 60°C.

EVALUATION OF RATE CONSTANTS.

The rate constants for the termination reactions of polymethyl methacrylate radicals with cupric chloride and cupric bromide were evaluated by measuring the value of k_x/k_p from a study of the period of acceleration following the complete inhibition.

As discussed earlier (pages 22 - 24) k_x/k_p can be determined from kinetic studies in two ways.

(1) From equation (22)

$$-\frac{1}{\phi_t} + \log\frac{1+\phi_t}{1-\phi_t} = k_x[R]_s t + A \qquad (22)$$

The left hand side of equation (22) is plotted against t for measured values of ϕ_t and corresponding reaction times. The slope of this line is equal to $k_x[R]_s$, and substituting this value in equation (26),

$$\frac{k_x}{k_p} = \frac{k_x[R]_s[M]}{(Rp)_s},$$

the ratio k_x/k_p can be determined.

(11) From equation (35)

$$k_x = \frac{\left\{(1-\phi_t^2)/\phi_t\right\}(Ik_t)^{\frac{1}{2}}}{[CuCl_2]_o(1-F)^{k_x/k_p}} \qquad (35)$$

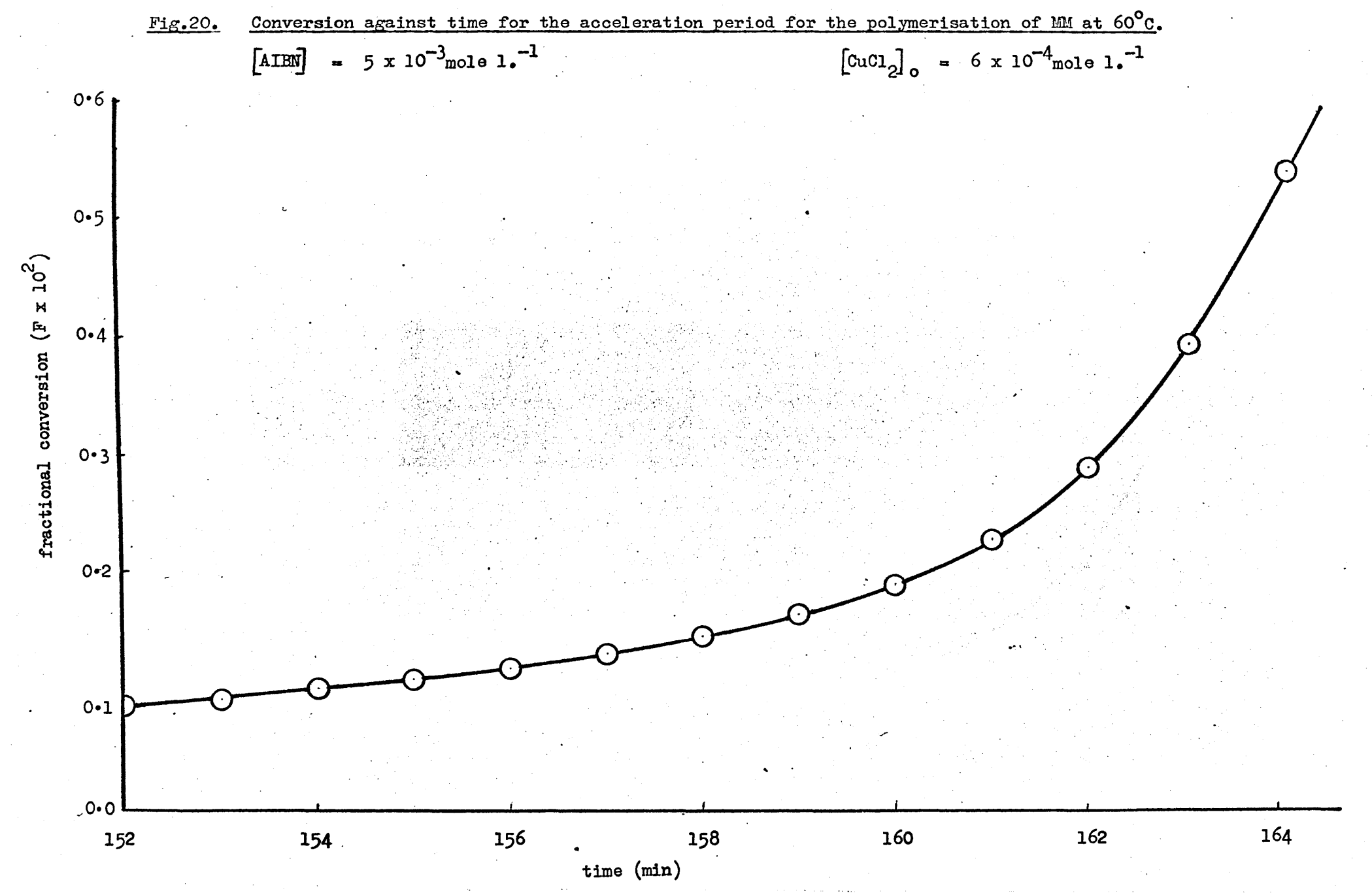
Using measured values of ϕ_t and F, k_x/k_p may be determined from the slope of the line obtained by plotting the logarithm of either $(1-\phi_t^2)/\phi_t$, I or $[CuCl_2]_o^{-1}$ against the logarithm of $(1-F)$ for fixed values of the remaining two variables.

RATE CONSTANTS FOR THE CUPRIC CHLORIDE REACTION

The initial experiments were carried out at 60°C. Polymerisation versus time curves for reactions with low and high initiator concentrations are shown in figs. 20 and 21 respectively, the initial cupric chloride concentrations being

Fig.20. Conversion against time for the acceleration period for the polymerisation of MM at 60°C.

$[AIBN] = 5 \times 10^{-3}$ mole $l.^{-1}$ $[CuCl_2]_o = 6 \times 10^{-4}$ mole $l.^{-1}$



6×10^{-4} mole $l.^{-1}$ in each case. These curves are approximately $\frac{1}{2}$ size scale of those used for measurements of ϕ_t and F. Due to the slope of the % polymerisation versus time curves, it is difficult to determine accurately the values of the time and fractional conversion corresponding to any value of ϕ_t if it is less than 0·2 or greater than 0·8. Thus values of ϕ_t in the range 0·2 to 0·8 were used in evaluating k_x. Fig. 22 shows the left hand side of equation (22) plotted against time, and the two plots (a) and (b) refer to experiments with low and high initiator concentrations shown in figs. 20 and 21 respectively. Calculation of the functions from dilatometric results is shown in the Appendix. In general, greater linearity was obtained at lower initiator concentrations, possibly due to inaccuracies caused by the shorter acceleration periods at higher initiator concentrations; consequently, ϕ_t values increase more rapidly and greater accuracy in determining ϕ_t and the corresponding time values would be necessary to obtain the same overall experimental error. The slopes of the lines (a) and (b) in fig. 22 were found to be 0·028 and 0·042 sec^{-1} respectively, which substituted in equation (26) give values of 1010 and 800 respectively for k_x/k_p.

A plot of $\log (1 - \phi_t^2)/\phi_t$ against $\log (1 - F)$ for fixed rates of initiation and cupric chloride concentrations is given in fig. 23. The initiator concentration was 1×10^{-2} mole $l.^{-1}$ for both experiments, while the initial cupric chloride concentration was $1{\cdot}30 \times 10^{-3}$ mole $l.^{-1}$ for curve (a) and $4{\cdot}35 \times 10^{-4}$ mole $l.^{-1}$ for curve (b). Both plots are reasonably linear and represent the type of curves found with

Fig.22 Graph of l.h.s. of equation (22) against t for the polymerisation of methyl methacrylate in the presence of 6×10^{-4} mole $l.^{-1}$ cupric chloride and (a) 5×10^{-3} mole $l.^{-1}$ AIBN; (b) 2×10^{-2} mole $l.^{-1}$ AIBN.

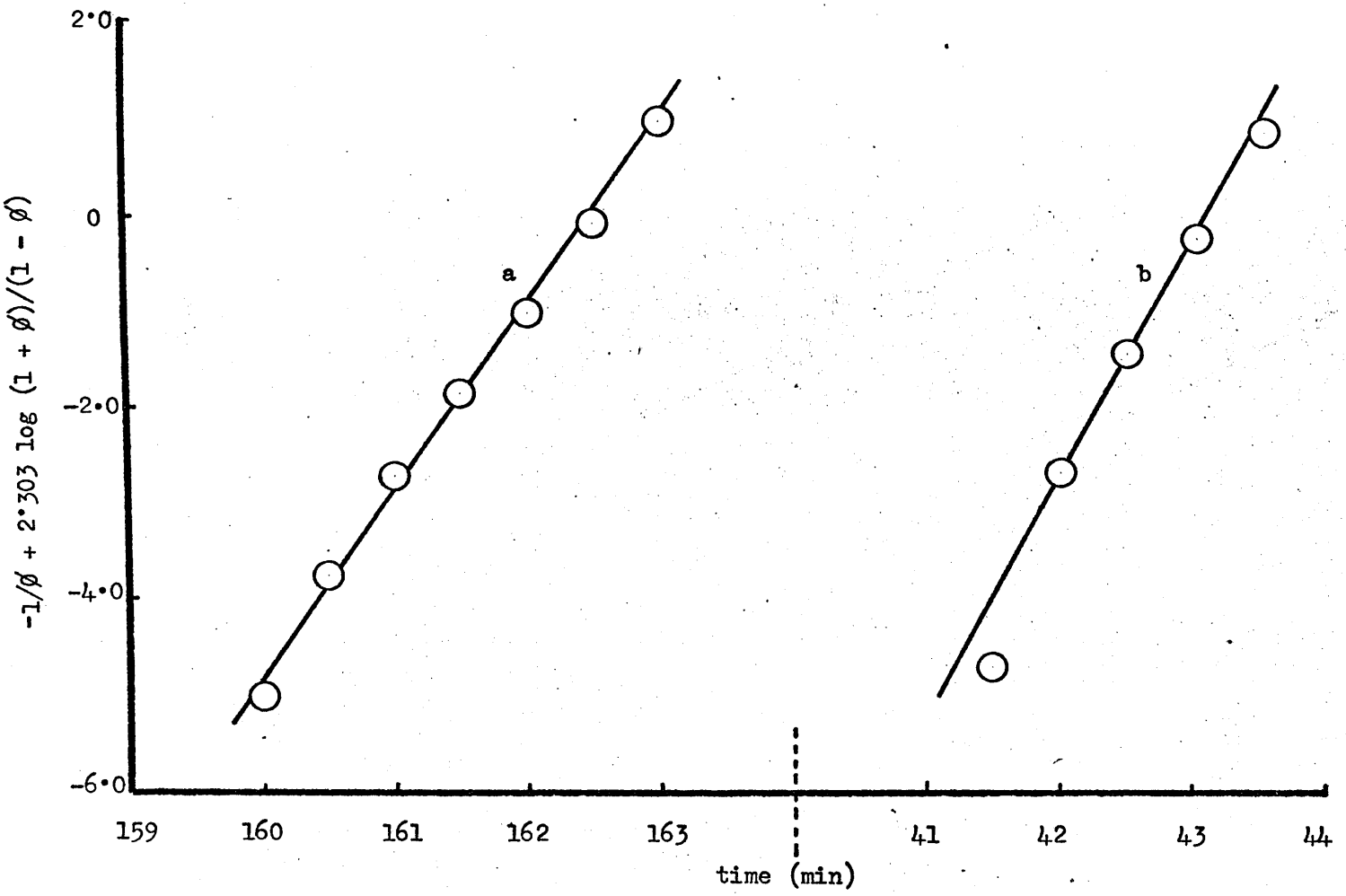
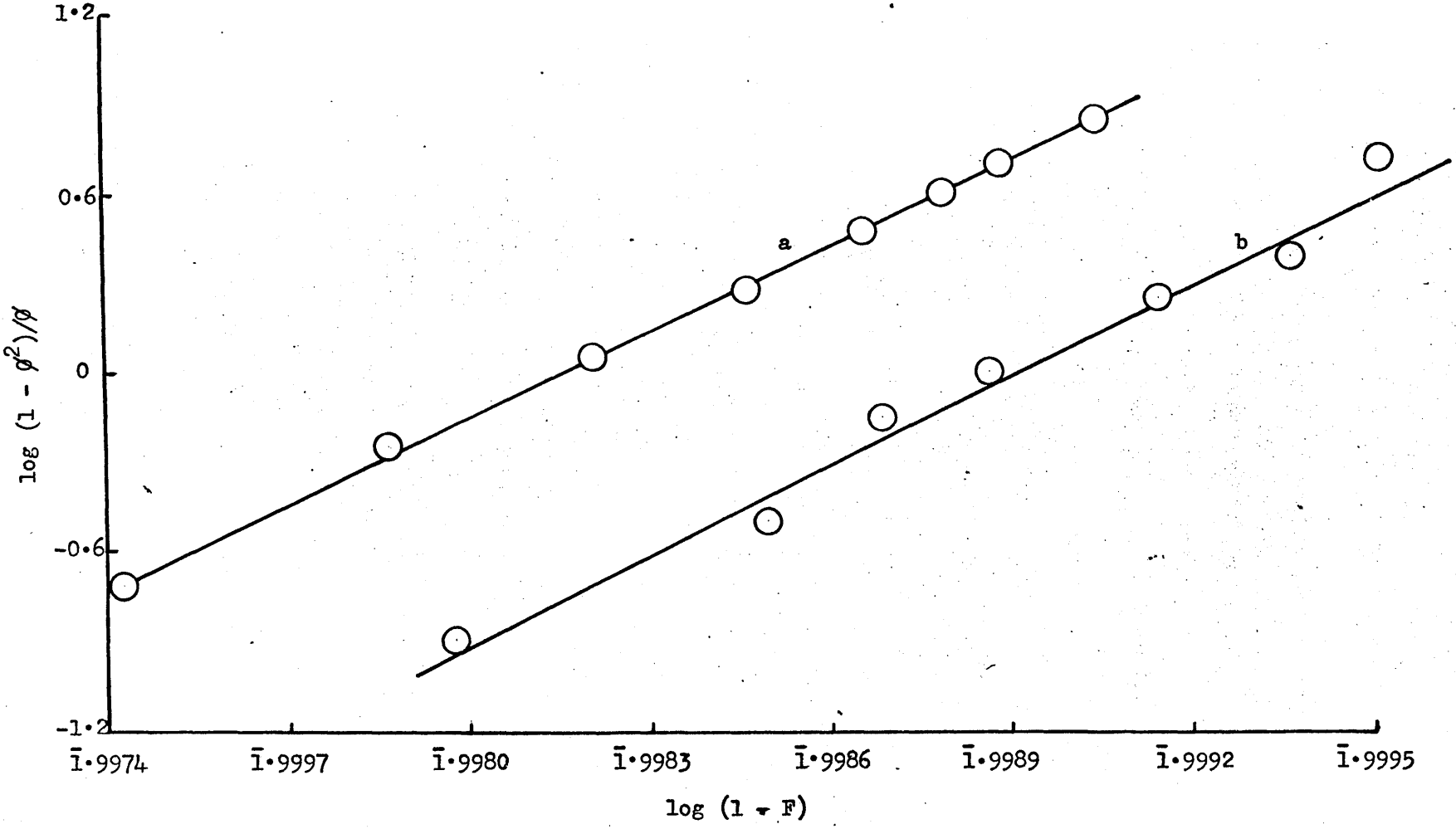


Fig.23 Graph of log $(1-\phi^2)/\phi$ against log (1-F) for the polymerisation of methyl methacrylate in the presence of 10^{-2}mole $l.^{-1}$ AIBN and (a) $1{\cdot}3 \times 10^{-3}$mole $l.^{-1}$ cupric chloride; (b) $4{\cdot}35 \times 10^{-4}$mole $l.^{-1}$ cupric chloride.



AIBN concentrations of 0·5 to 1·5 x 10^{-2} mole $l.^{-1}$ and cupric chloride concentrations of 4·35 to 13·04 x 10^{-4} mole $l.^{-1}$. Values obtained from curves (a) and (b) are 990 and 1020 respectively for k_x/k_p.

In fig. 24 log $[CuCl_2]_o$ is plotted against log (1 - F) for fixed values of ϕ_t, viz: 0·3 for curve (a) and 0·5 for curve (b); the initiator concentration being 1 x 10^{-2} mole $l.^{-1}$ in every case. It is impossible to obtain accurate gradients from such plots because of the scatter of points, but values accurate to within a factor of 2 are possible. The gradients of lines (a) and (b) in fig. 24 give values for k_x/k_p of 1030 and 990 respectively, in reasonable agreement with the previous values.

Plots of log I against log (1 - F) for fixed values of ϕ_t and $[CuCl_2]_o$ show an even greater scatter of points and no gradient measurements are possible.

A summary of the values of k_x/k_p obtained from plots of the type shown in fig. 22 and fig. 23 are listed in Table 6.

Table 6 /-

Fig. 24 Graph of $-\log [CuCl_2]_o$ against log (1-F) for the polymerisation of methyl methacrylate in the presence of 10^{-2} mole $l.^{-1}$ AIBN.

In curve a, $\phi_t = 0.3$ and in curve b, $\phi_t = 0.5$

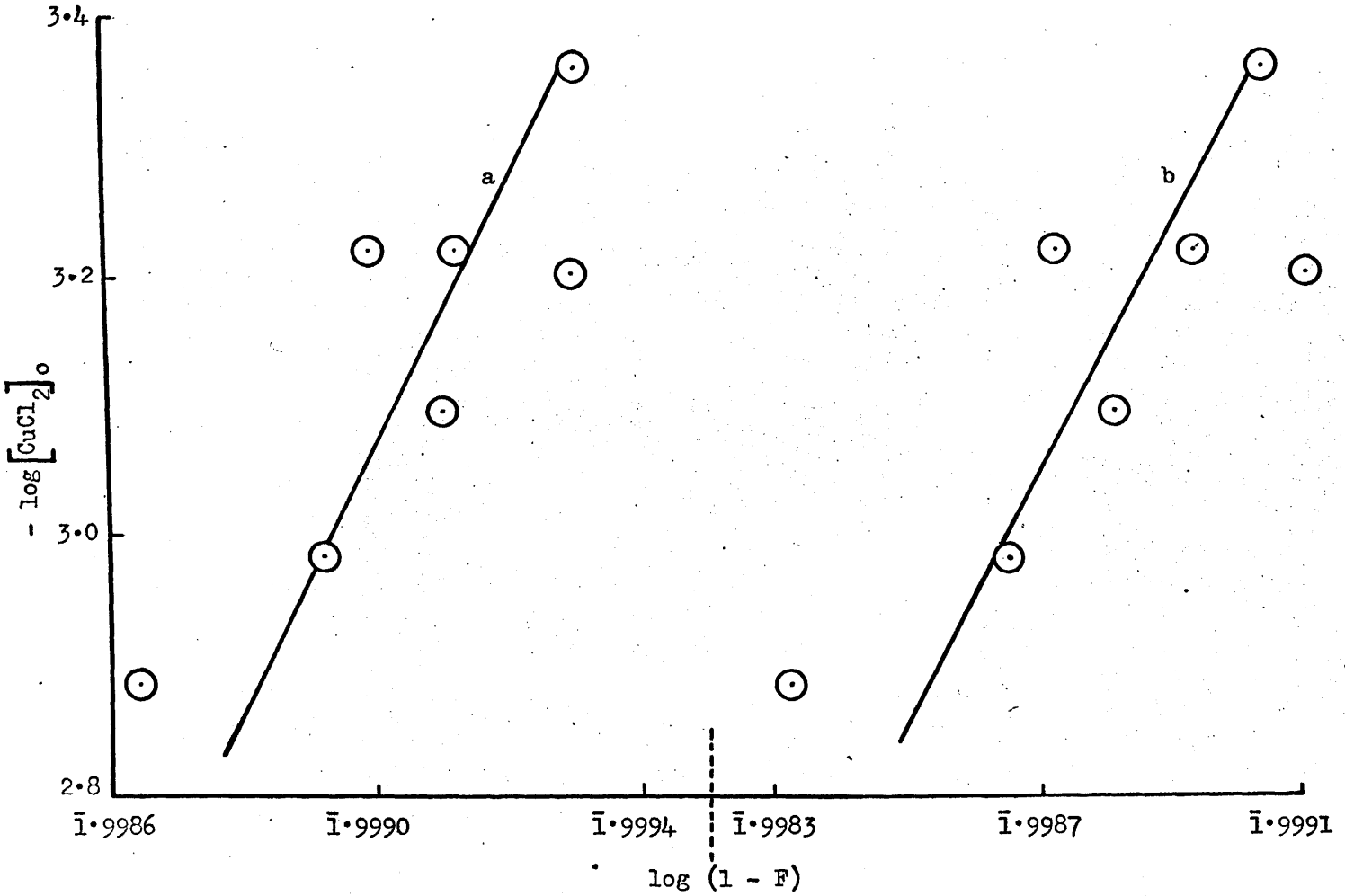


Table 6 - Values of k_x/k_p determined using equations (22) and (35), with data from the polymerisation of methyl methacrylate in the presence of various concentrations of AIBN and cupric chloride.

[AIBN] mole $l.^{-1}$ ($\times 10^2$)	$[CuCl_2]_o$ mole $l.^{-1}$ ($\times 10^4$)	Values of k_x/k_p Using eqn.(22)	Using eqn.(35)
1·0	4·35	1020	980
1·0	6·25	1200	1050
1·0	8·04	1210	1010
1·0	10·43	1160	1010
1·0	13·04	980	990
0·5	6·0	1010	1100
0·75	6·0	1090	1010
1·0	6·0	1200	1050
1·5	6·0	900	970
2·0	6·0	800	800

If the values at high initiator concentrations are omitted for the reasons given previously, the average value of k_x/k_p at 60°C is 1050.

RATE CONSTANTS FOR THE CUPRIC BROMIDE REACTION

Similar experiments were carried out using cupric bromide as inhibitor.

Compared with the experiments with cupric chloride, the acceleration periods were much shorter, and using the cylindrical

shaped dilatometer bulbs non isothermal conditions were obtained. To eliminate the 'self-heating' effect, very thin disc-shaped dilatometers were used to allow good heat transfer throughout the dilatometer. A conversion/time plot of the acceleration period is shown in fig. 25 for an initiator concentration of $1 \cdot 10^{-2}$ mole $l.^{-1}$ and an initial cupric bromide concentration of $6 \cdot 0 \times 10^{-4}$ mole $l.^{-1}$. The curve obtained under non-isothermal conditions at the same concentrations is also shown in fig. 25. In the reactions to evaluate the ratio k_x/k_p lower initiator concentrations ($< 1 \times 10^{-2}$ mole $l.^{-1}$) were used to reduce the generation of heat at the onset of polymerisation.

The curves obtained from plots using equation (22) and equation (35) were less linear than those obtained using cupric chloride, possibly due to the greater experimental error in measurements over shorter acceleration periods. However, by considering values of ϕ_t between 0·3 and 0·7, reasonable straight lines were obtained.

Fig. 26 refers to a plot of the left hand side of equation (22) against time. Plot (a) refers to an initiator concentration of 5×10^{-3} mole $l.^{-1}$ and an initial cupric chloride concentration of 3×10^{-4} mole $l.^{-1}$; plot (b) refers to an initiator concentration of $3 \cdot 5 \times 10^{-3}$ mole $l.^{-1}$ and an initial cupric chloride concentration of 4×10^{-4} mole $l.^{-1}$. The calculation of the functions from dilatometric data is shown in the Appendix. The slopes of the lines (a) and (b) are 0·069 and 0·052 sec^{-1} respectively. Substituting these

Fig.25. Conversion against time for the acceleration period for the polymerisation of MM at 60°C.

$[AIBN] = 1 \times 10^{-2}$ mole $l.^{-1}$ $[CuBr_2]_o = 6 \times 10^{-4}$ mole $l.^{-1}$

– – – – shows the curve obtained under non-isothermal conditions.

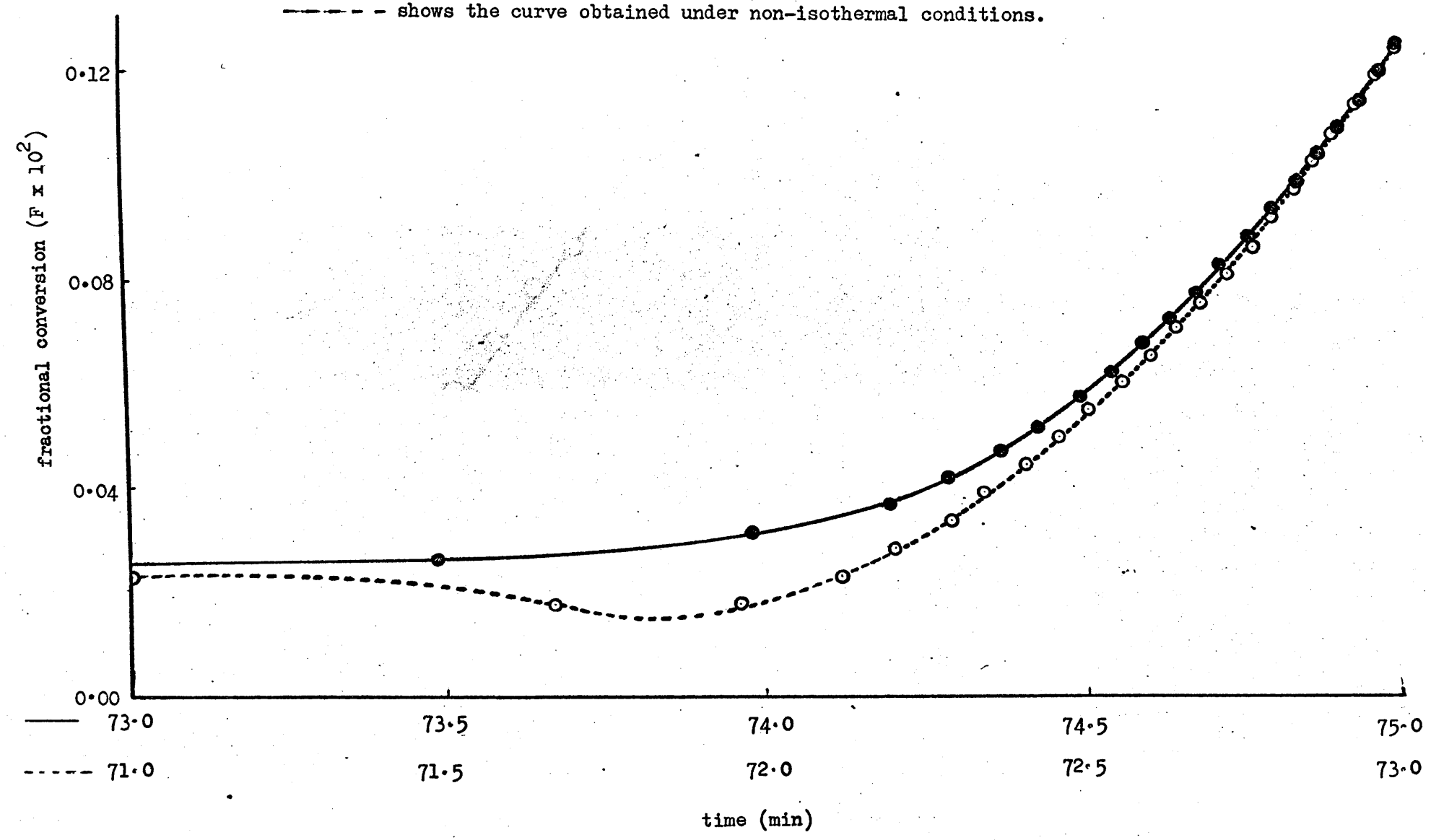
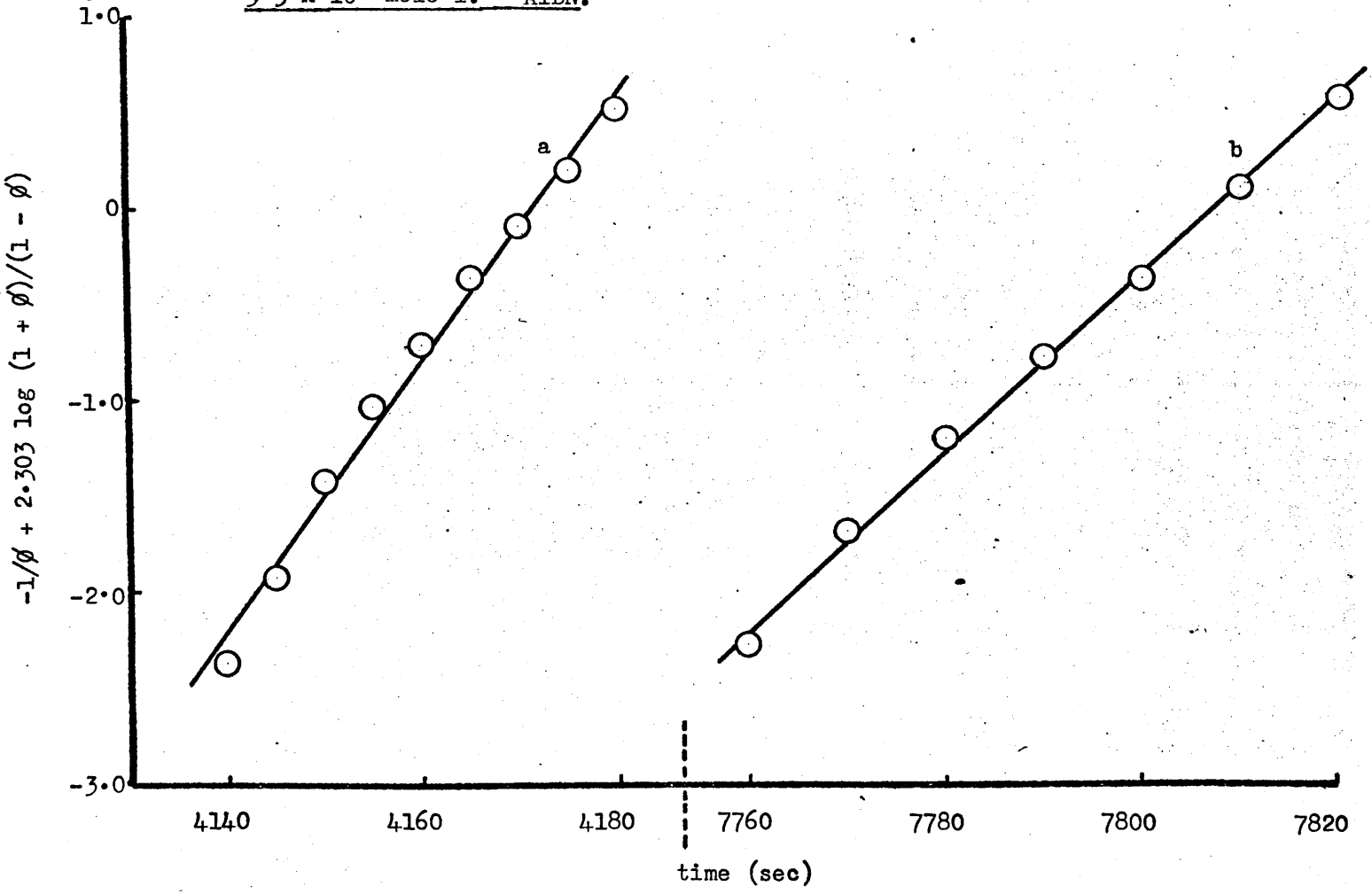


Fig.26 Graph of the l.h.s. of equation (22) against t for the polymerisation of methyl methacrylate in the presence of (a) 3×10^{-4} mole $l.^{-1}$ cupric bromide and 5×10^{-3} mole $l.^{-1}$ AIBN: (b) 4×10^{-4} mole $l.^{-1}$ cupric bromide and $3{\cdot}5 \times 10^{-3}$ mole $l.^{-1}$ AIBN.



values in equation (26) gives values of 2450 and 2180 respectively for k_x/k_p.

Fig. 27 shows a plot of log $(1 - \phi_t^2)/\phi_t$ against log (1 - F) for the same experiments plotted in fig. 26. Curves (a) and (b) give values of 2120 and 2050 respectively for k_x/k_p. The curves shown in fig. 26 and fig. 27 are representative of those found for initiator concentrations of $3{\cdot}5 - 8{\cdot}0 \times 10^{-3}$ mole $l.^{-1}$ and initial cupric chloride concentrations of $1{\cdot}8 - 6{\cdot}0 \times 10^{-4}$ mole $l.^{-1}$. Plots of log $[CuBr_2]_o$ and log I against log (1 - F) show a wide scatter of points, as with the experiments with cupric chloride, and no gradient measurements could be made from them.

A summary of the values of k_x/k_p obtained from plots of the type shown in fig. 26 and fig. 27 are listed in Table 7.

Table 7 /-

Fig.27 Graph of log $(1 - \phi^2)/\phi$ against log (1 - F) for the polymerisation of methyl methacrylate in the presence of (a) 3×10^{-4} mole $l.^{-1}$ cupric bromide and 5×10^{-3} mole $l.^{-1}$ AIBN; (b) 4×10^{-4} mole $l.^{-1}$ cupric bromide and $3{\cdot}5 \times 10^{-3}$ mole $l.^{-1}$ AIBN.

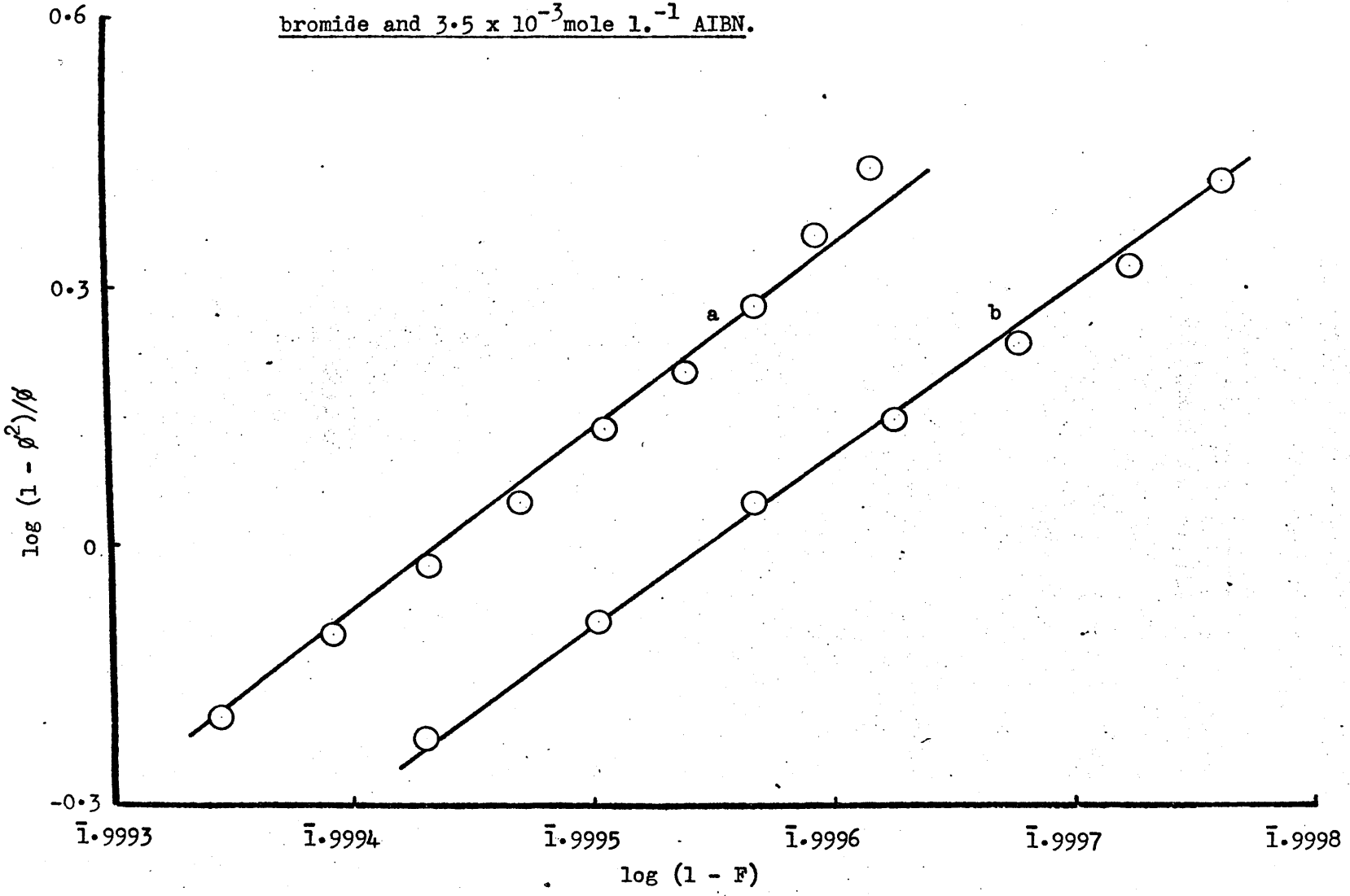


Table 7 - Values of k_x/k_p determined using equations (22) and (35), with data from the polymerisation of methyl methacrylate in the presence of various concentrations of AIBN and cupric bromide.

[AIBN] mole $l.^{-1}$ (x 10^3)	$[CuBr_2]_o$ mole $l.^{-1}$ (x 10^4)	Values of k_x/k_p Using eqn.(22)	Using eqn.(35)
5·0	1·8	2220	1950
5·0	3·0	2450	2120
5·0	4·0	2360	2220
5·0	5·0	1800	1900
5·0	6·0	2430	2020
3·5	4·0	2180	2050
6·5	4·0	2550	2450
8·0	4·0	2250	2080

The average value of k_x/k_p is 2190.

VALUES OF k_x

Using the value of k_p obtained by Matheson et al.[41] corrected for termination by disproportionation, viz: 734 $l.mole^{-1}sec^{-1}$, the following values for k_x are obtained.

Inhibitor	k_x ($l.mole^{-1}sec^{-1}$)
$CuCl_2$	7.7×10^5
$CuBr_2$	$1{\cdot}61 \times 10^6$

DETERMINATION OF ACTIVATION ENERGIES

The velocity coefficient, k, of a reaction is related to the energy of activation by the expression

$$k = Ae^{-E/RT} ,$$

where

A = Collision Frequency Factor

E = Activation Energy

T = Temperature (degree absolute)

R = Molar Gas Constant.

$E_p - E_x$.

The following expressions may be written for k_p and k_x, the velocity coefficients for the propagation reaction and the termination reaction involving cupric salt respectively.

$$k_p = A_p e^{-E_p/RT} \qquad k_x = A_x e^{-E_x/RT} .$$

Therefore

$$\frac{k_x}{k_p} = \frac{A_x}{A_p} e^{(E_p - E_x)/RT}$$

or

$$\ln \frac{k_x}{k_p} = \ln \frac{A_x}{A_p} + \frac{\Delta E}{RT}$$

where

$$\Delta E = E_p - E_x \ .$$

Thus a plot of $\log_{10} k_x/k_p$ against $1/T$ gives a line of slope $\Delta E/2{\cdot}3R$.

k_x/k_p values were measured, using equations (22) and (35) as described in the previous section, at different temperatures between 40°C and 72°C.

Those studies were made on the polymerisation of methyl methacrylate in the presence of cupric chloride and cupric bromide, and the results are shown in Tables (8) and (9) respectively. In both cases the values quoted for k_x/k_p at 60°C are average values calculated from the results in Tables (6) and (7).

Table 8 /-

Table 8 - A list of values of k_x/k_p using equations (22) and (35) with data from the polymerisation of methyl methacrylate in the presence of cupric chloride at various temperatures.

Temp. °C	[AIBN] x 10^3 mole $l.^{-1}$	$[CuCl_2]_o$ x 10^4 mole $l.^{-1}$	k_x/k_p using eqn.(22)	k_x/k_p using eqn.(35)
40	60	1	2370	2540
40	60	2	1080	1720
40	60	3	1020	1160
60	5 - 15	4 - 13	1086	1019
70	0·5	1·25	2180	2230
70	0·5	1·66	1880	1560
72	0·5	0·83	1500	1550
72	0·5	1·4	2830	2600

Table 9 - A list of values of k_x/k_p using equations (22) and (35) with data from the polymerisation of methyl methacrylate in the presence of cupric bromide at various temperatures.

Temp. °C	[AIBN] x 10^3 mole $l.^{-1}$	$[CuBr_2]_o$ x 10^4 mole $l.^{-1}$	k_x/k_p using eqn.(22)	k_x/k_p using eqn.(35)
40	60	1·0	2200	1900
40	60	2·0	1350	1470
40	60	3·0	1730	1700
50	25	4·0	1670	1930
50	25	6·0	2200	2310
50	25	7·33	1820	1950
60	3·5 - 8·0	1·8 - 6·0	2280	2100
70	1·0	1·0	3980	3020
70	0·5	0·75	2830	2610
70	0·5	1·0	2750	2460

The results are shown graphically in fig. 28 and 29 for the reaction involving cupric chloride and cupric bromide respectively.

No accurate determination of ΔE is possible from the results for the reaction involving cupric chloride as illustrated in fig. 28 . There appears to be little variation in log k_x/k_p with temperature, however, and thus ΔE is

Fig.28 - Determination of ΔE for the polymerisation of methyl methacrylate initiated by AIBN in the presence of cupric chloride.

● and ○ refer to values obtained using equations (22) and (35) respectively.

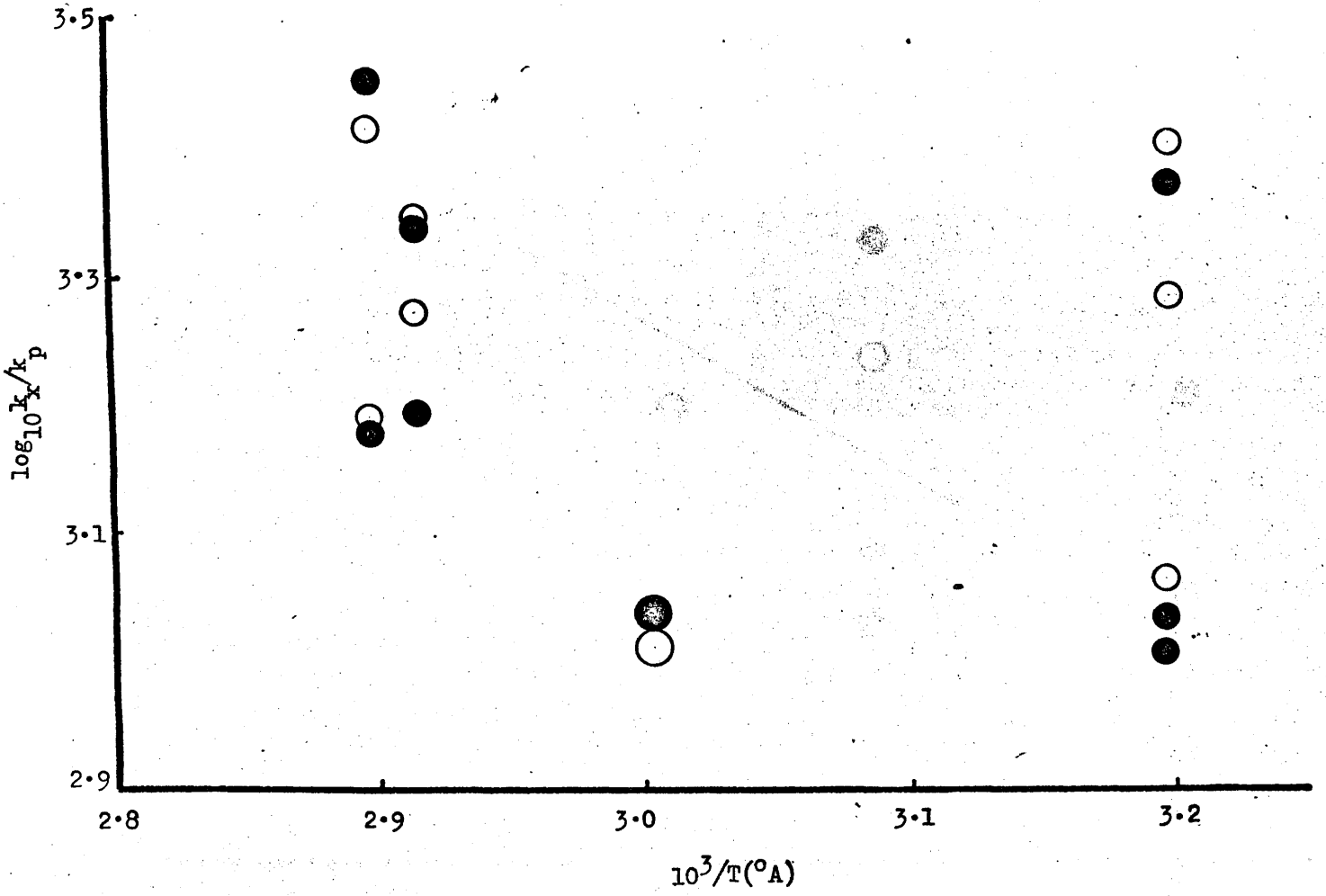
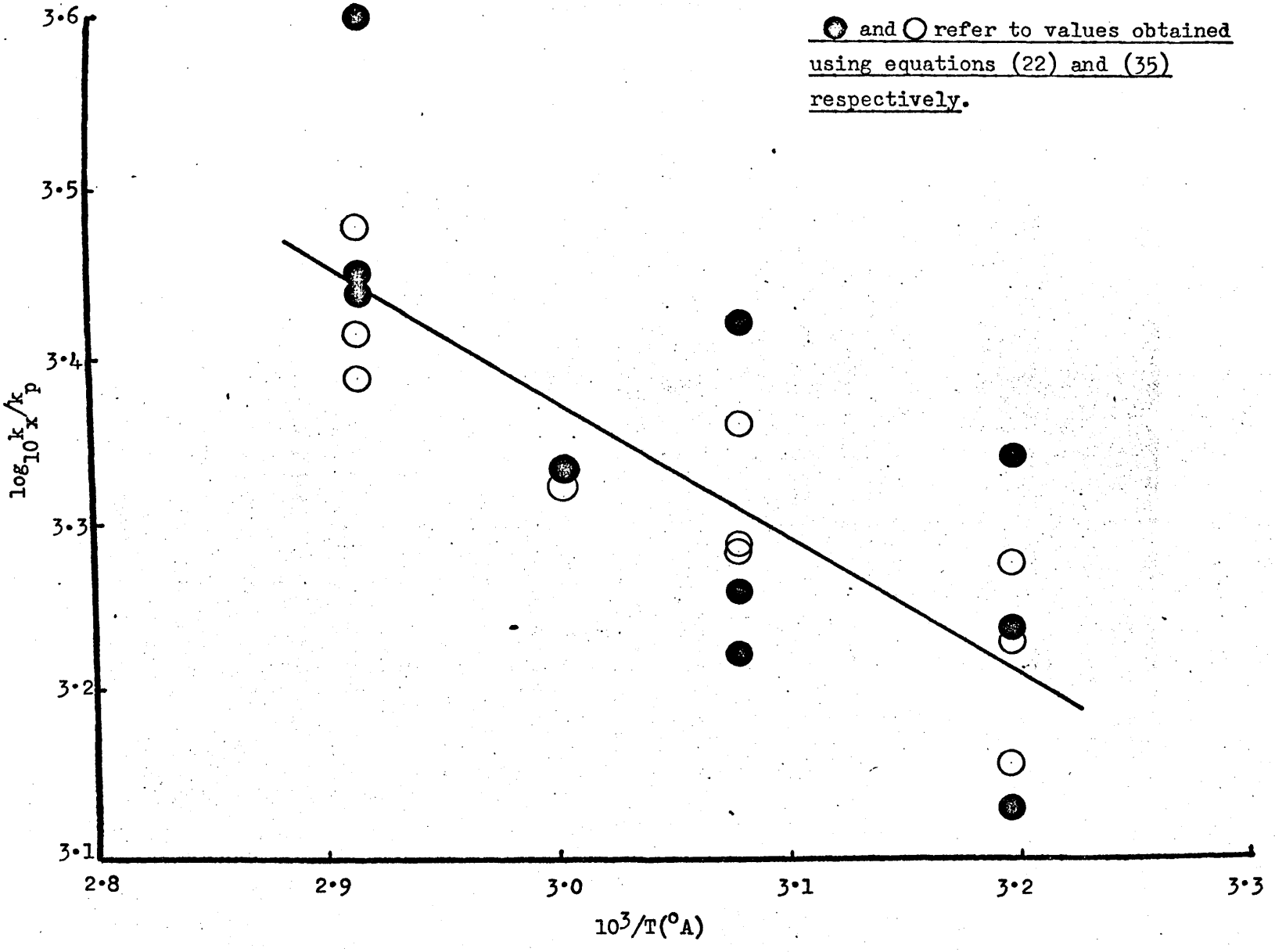


Fig.29 - Determination of ΔE for the polymerisation of methyl methacrylate initiated by AIBN in the presence of cupric bromide.



approximately equal to zero.

The value of ΔE, calculated from the slope of the curve in fig.29 for the reaction involving cupric bromide, is - 3·6 kcal.

Using the value of E_p of 6 kcal calculated by Matheson et al.[41], the values of E_x for the reactions are:

Inhibitor	E_x(kcal)
Cupric chloride	approx. 6
Cupric bromide	9·6

OVERALL ACTIVATION ENERGY, E_o

From equation (2)

$$Rp = \frac{k_p I^{\frac{1}{2}} [M]}{k_t^{\frac{1}{2}}}$$

As the monomer concentration remains sensibly constant during the initial stages of polymerisation, then

$$\log_{10} \frac{Rp}{[AIBN]^{\frac{1}{2}}} = K - \frac{E_o}{2{\cdot}3\ RT} ,$$

where K is a constant and $E_o = \frac{1}{2}E_i + E_p - \frac{1}{2}E_t$. Thus a plot of $\log_{10} Rp/[AIBN]^{\frac{1}{2}}$ against $1/T$ will have a slope of $-E_o/2{\cdot}3R$.

Rates of polymerisation were measured at different temperatures between 40°C and 70°C and the results are shown graphically in fig. 30. From the slope of the curve, the overall activation energy was calculated as

$$E_o = 20{\cdot}5 \text{ kcal.}$$

ACTIVATION ENERGY OF THE INITIATION REACTION, E_i.

In this case

$$\ln k_i = \ln A_i - \frac{E_i}{RT}$$

Rates of initiation were measured at different temperatures between 40°C and 70°C from the length of inhibition periods obtained using cupric chloride and bromide respectively as radical scavengers. Fig. 31 refers to a plot of $\log_{10} k_i$ against 1/T for the values obtained for k_i using the cupric salts as radical scavengers in the AIBN initiated polymerisation of methyl methacrylate. The activation energy, measured from the slope of the plot is

$$E_i = 32{\cdot}9 \text{ kcal.}$$

Fig.30 - Determination of E_o for the polymerisation of methyl methacrylate initiated by AIBN.

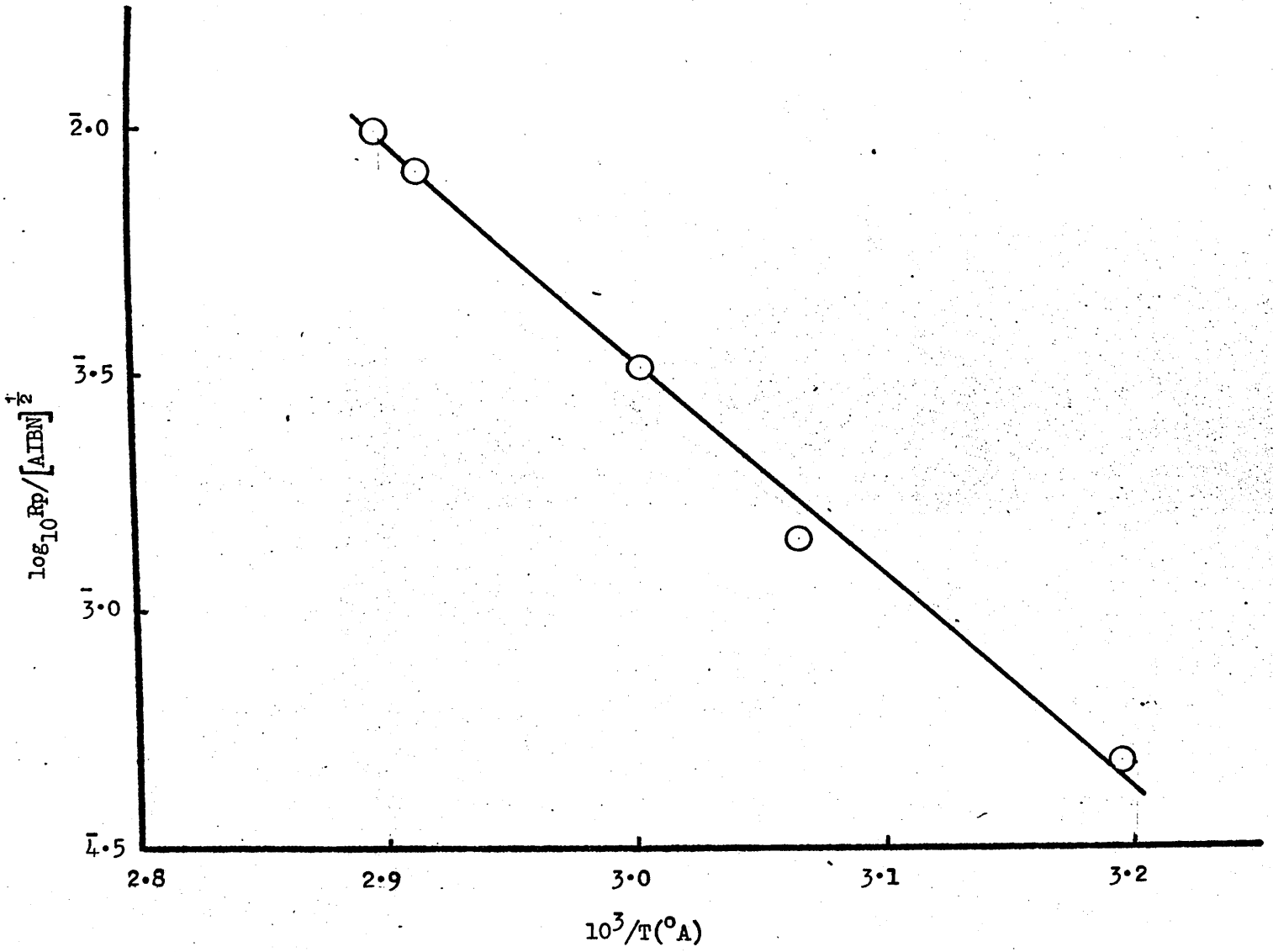
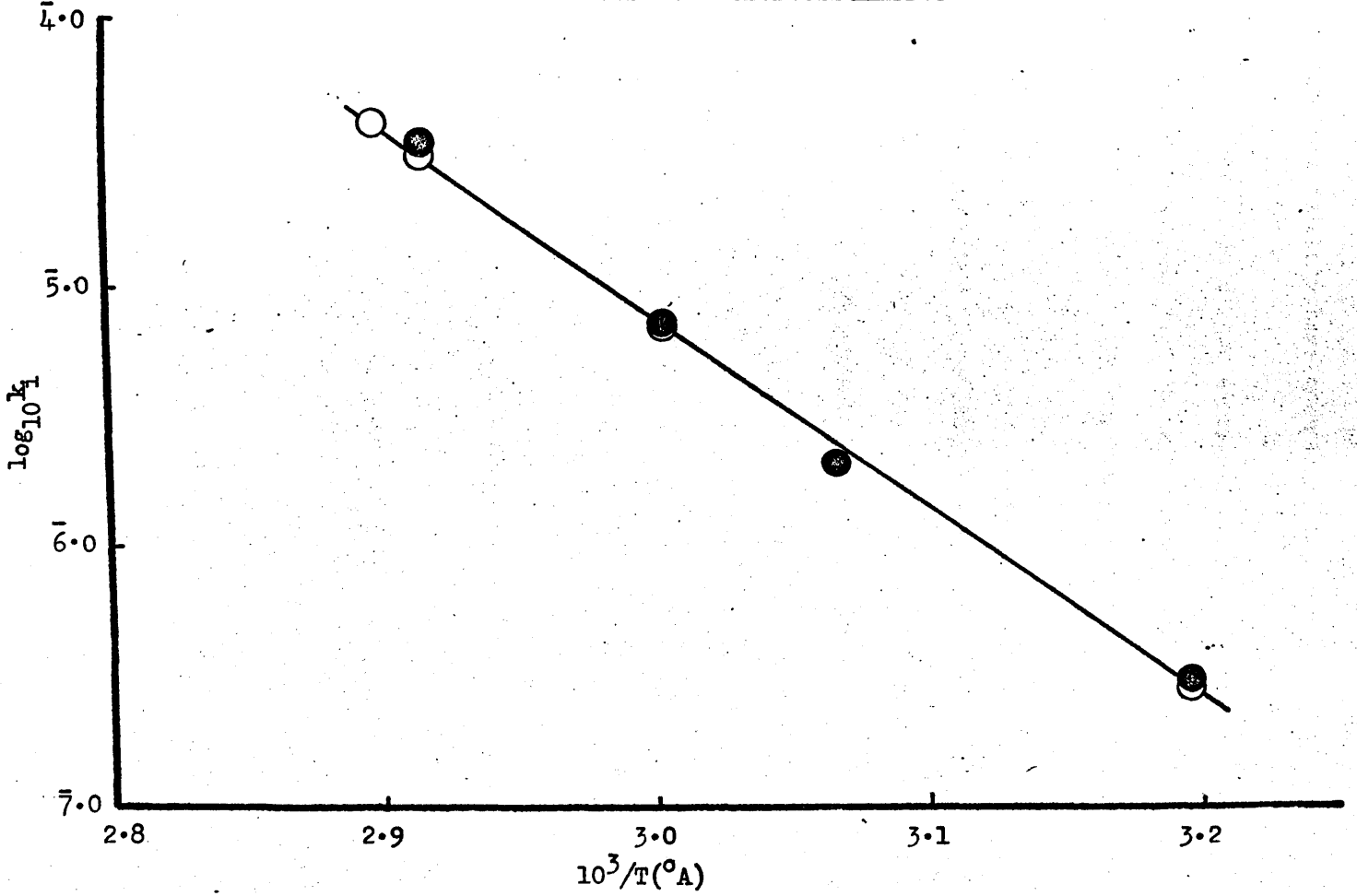


Fig.31 - Determination of E_i for the polymerisation of methyl methacrylate initiated by AIBN.

● and ○ refer to values of k_i obtained using cupric bromide and cupric chloride respectively as inhibitors.



EFFECT OF H_2O ON THE $CuCl_2$ TERMINATION REACTION

The effects of small quantities of water on the cupric chloride inhibited polymerisation of methyl methacrylate in dimethylformamide solution have been examined.

The polymerisations were carried out at 60°C with constant $[M]$ = 8·06 mole $l.^{-1}$. To maintain homogeneous conditions in the dilatometer, only small quantities of H_2O could be added.

Fig. 32 illustrates the effect of H_2O on the % polymerisation versus time curve of the acceleration period. Curves a, b and c refer to H_2O concentrations of zero, 0·55 and 1·10 mole $l.^{-1}$ respectively. In each case the initial initiator and cupric chloride concentrations were 8×10^{-2} and 6×10^{-4} mole $l.^{-1}$ respectively. The added water appears to reduce the length of the inhibition period and cause a substantial increase in the length of the acceleration period. The final rate of polymerisation is not effected by the added H_2O.

EFFECT OF ADDED H_2O ON k_x/k_p.

Fig. 33 shows plots of $\log (1 - \phi_t^2)/\phi_t$ against $\log (1 - F)$ for the polymerisations with varying amounts of H_2O. As before, curves a, b and c refer to H_2O concentrations of zero, 0·55 and 1·10 mole $l.^{-1}$ respectively, the initial initiator and cupric chloride concnetrations in each case being 8×10^{-2} and 6×10^{-4} mole $l.^{-1}$ respectively. The

Fig.32 - The polymerisation of methyl methacrylate at 60°C in the presence of 8×10^{-3} mole $l.^{-1}$ AIBN, 6×10^{-4} mole $l.^{-1}$ cupric chloride and (a) zero H_2O; (b) 0·55 mole $l.^{-1}$ H_2O; (c) 1·10 mole $l.^{-1}$ H_2O.

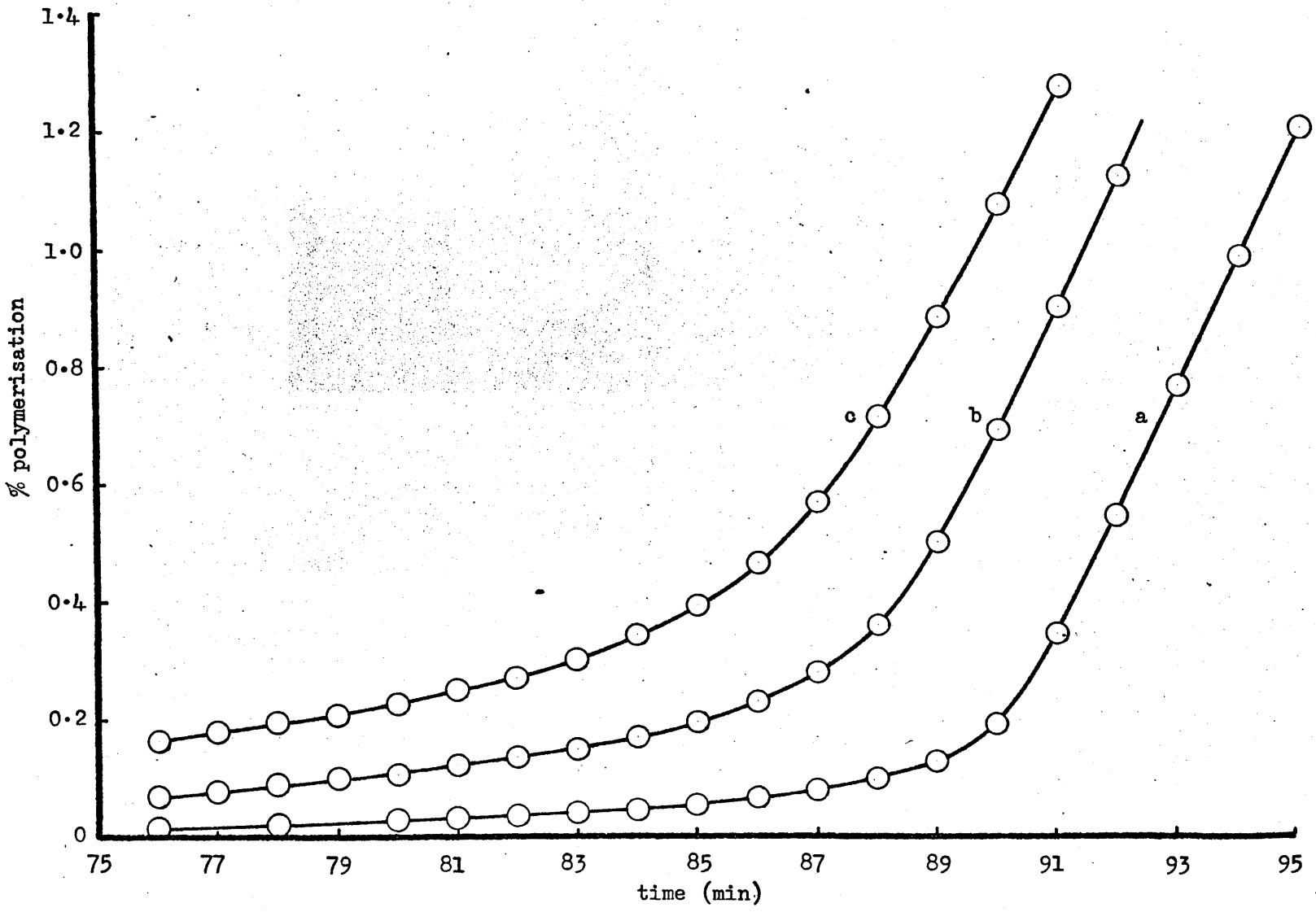
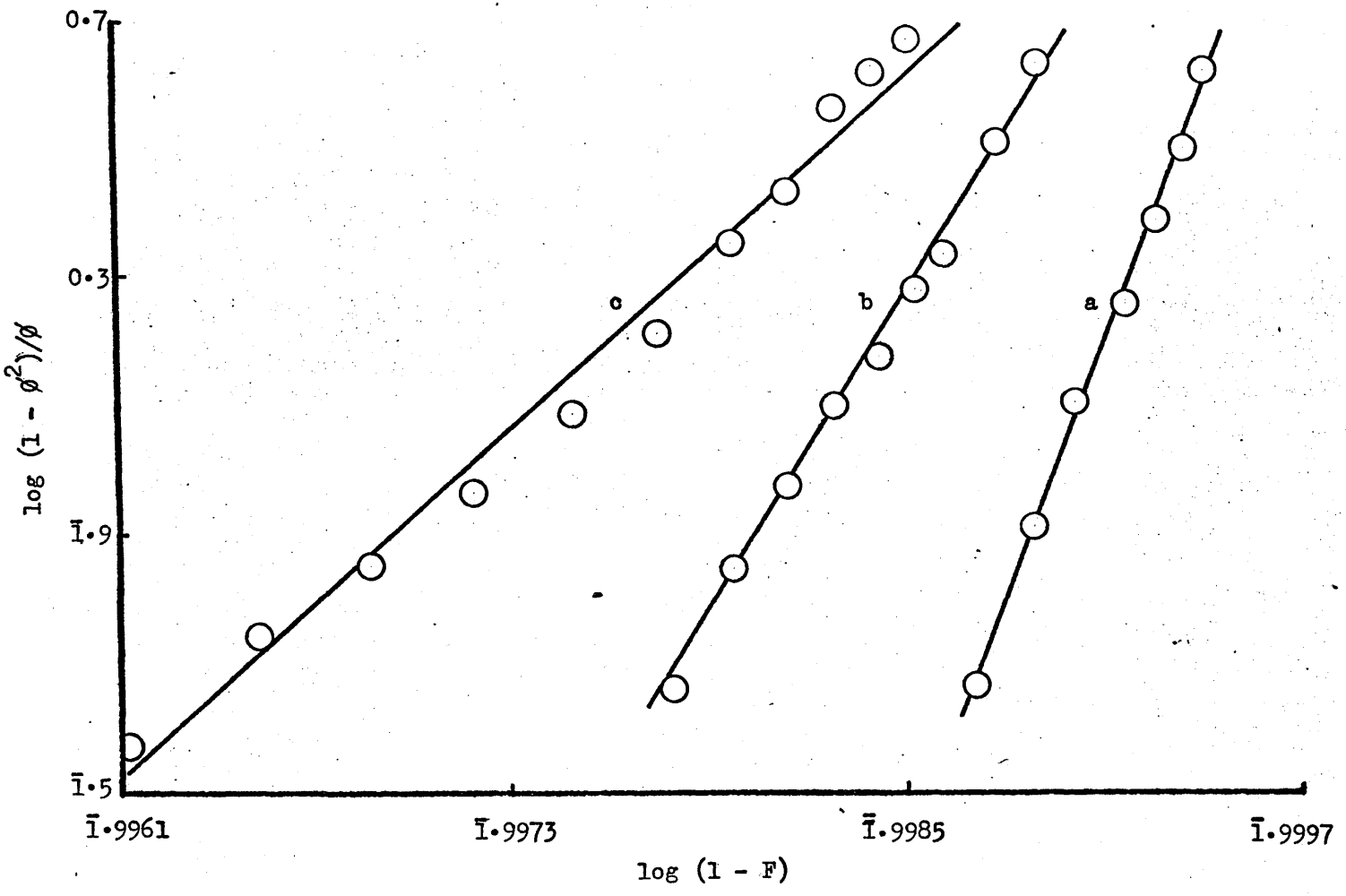


Fig.33 - The effect of H_2O on the value of k_x/k_p for the polymerisation of MM in the presence of 8×10^{-3} mole $l.^{-1}$ AIBN and 6×10^{-4} mole $l.^{-1}$ $CuCl_2$.

H_2O concentrations are 0, 0.55 and 1.10 mole $l.^{-1}$ for curves a, b and c respectively.



values of k_x/k_p, measured from the slopes are listed below.

$[H_2O]$ (mole $l.^{-1}$)	$\frac{k_x}{k_p}$
0	1290
0·55	820
1·10	470

The value, 1290, obtained in the absence of H_2O is slightly higher than the average value of 1050 obtained earlier (Table 6). The values shown above indicate a decrease in the value of k_x/k_p with added H_2O. As the value of k_p would not be expected to vary, the value of k_x appears to decrease by more than 50% by the addition of 1·10 mole $l.^{-1}$ H_2O.

THE EFFECT OF CUPRIC CHLORIDE ON THE POLYMERISATION OF METHYL METHACRYLATE IN THE ABSENCE OF SOLVENT.

As cupric chloride is almost completely insoluble in methyl methacrylate, no extensive kinetic studies could be carried out in the absence of solvent. However, the effect of cupric chloride on the polymerisation of methyl methacrylate initiated by AIBN at 70°C in the absence of solvent is illustrated in this experiment.

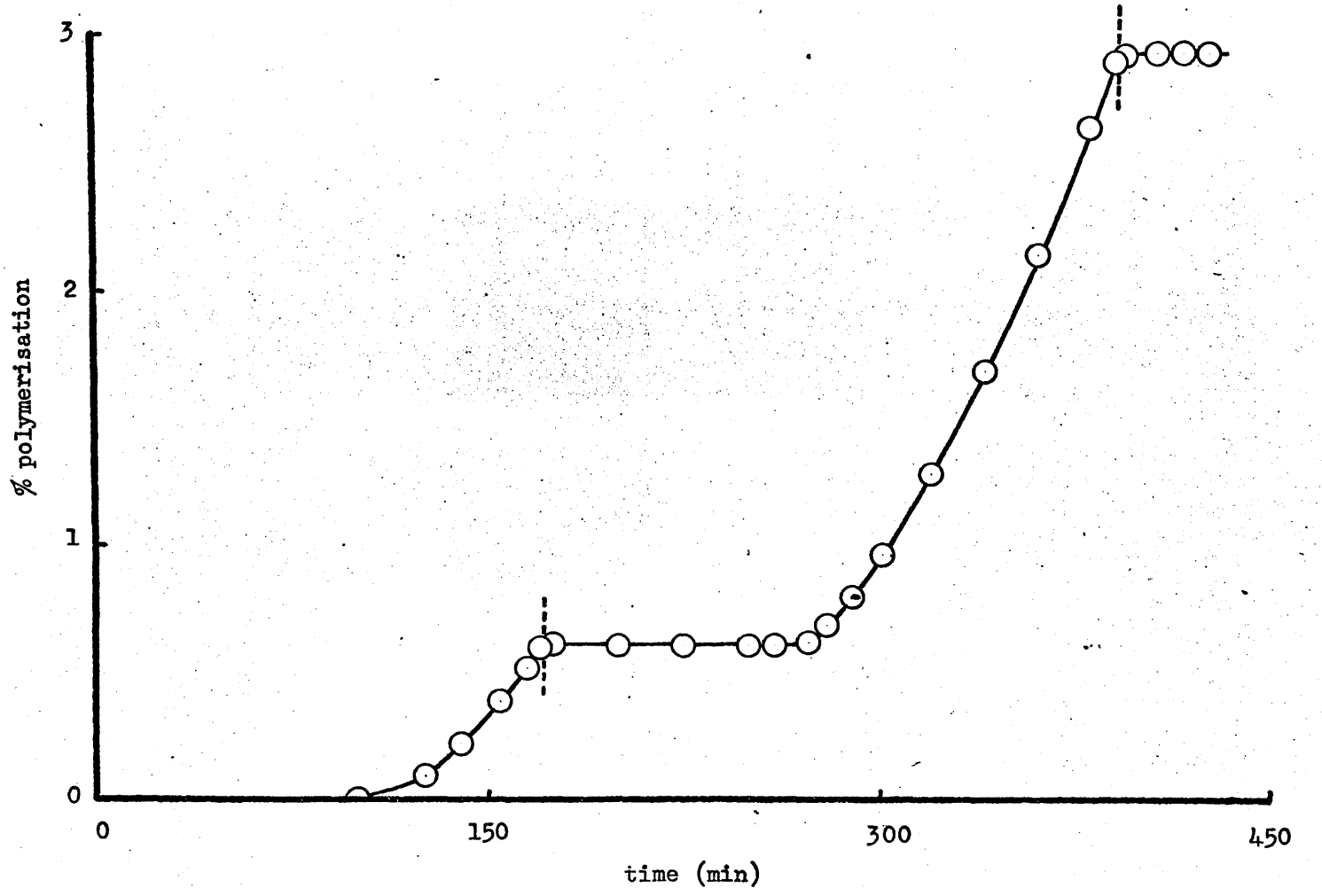
Cupric chloride in methyl methacrylate forms a type of suspension and the colouration of the solution suggests slight solubility.

The dilatometer used was of the normal bulb shape containing a magnetic follower, with a capillary of 2mm. diameter. AIBN was introduced into the dilatometer in standard chloreform solution, as before, and cupric chloride was added using an elongated dropping funnel. The required amount of methyl methacrylate was distilled 'in vacuo' into the dilatometer which was then isolated and the contents thawed, thoroughly mixed and placed in the thermostatic tank at 70°C.

Fig.34 shows the % polymerisation versus time plot for the reaction with an initial AIBN concentration of 1×10^{-3} mole $l.^{-1}$. The polymerisation is inhibited, the inhibition period being followed by a constantly changing rate of polymerisation. Also, as illustrated in fig.34 the polymerisation may be stopped at any time by reforming the suspension. This is formed by agitating the magnetic

Fig.34 - The polymerisation of methyl methacrylate initiated by 1 x 10^{-3} mole $l.^{-1}$ AIBN at 70°C in the presence of cupric chloride in the absence of solvent.

The vertical lines indicate the points at which the solution is stirred.



follower for approximately 15 second. It appears that the inhibition is caused by 'point solubilities' which exist in the suspension, and the length of the inhibition period is dependent on the rate of settling or diffusion of the cupric chloride particles.

THE EFFECT OF CUPRIC CHLORIDE ON THE POLYMERISATION OF METHYL METHACRYLATE USING ACETONITRILE AS SOLVENT

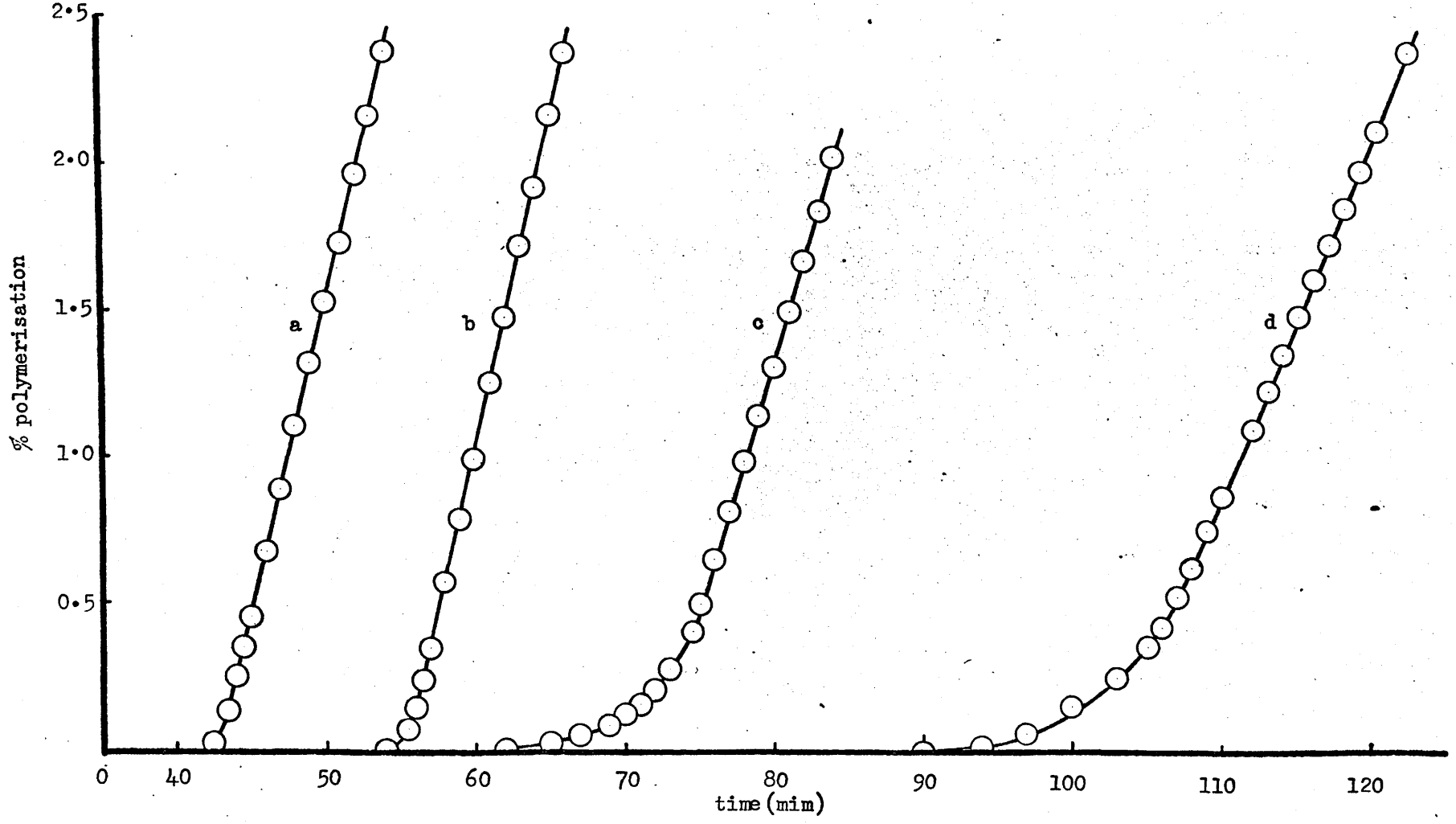
As before, the ratio of monomer to solvent was maintained at 90% to 10% by volume respectively, with the monomer concentration = 8·06 mole $l.^{-1}$ at 60°C. The cupric chloride acetonitrile solution was added to the dilatometer and outgassed in a similar manner to the DMF solution.

Fig. 35 shows typical % polymerisation versus time curves obtained in this system. In each case the initial AIBN concentration was $7·5 \times 10^{-3}$ mole $l.^{-1}$ and the initial cupric chloride concentrations varying from 4×10^{-4} to 10^{-3} mole $l.^{-1}$. In all cases, the polymerisation was inhibited, the inhibition period increased with increasing initial cupric chloride concentration. The length of the inhibition periods, however, are much shorter than with equivalent concentrations in the DMF system. Thus the rate of removal of the cupric species is much faster in the methyl cyanide system, if it is assumed that all the cupric salt is removed during the inhibition period.

There appears to be two separate reaction mechanisms occurring over the concentration range studied. Firstly, the reactions at initial cupric chloride concentrations below 6×10^{-4} mole $l.^{-1}$ (approximately), represented by curves (a) and (b) in fig. 35. In all reactions within this concentration, the inhibition period is followed by a very rapid acceleration in rate to the normal rate in the absence of inhibitor. The

Fig.35 – The polymerisation of MM initiated by $7{\cdot}5 \times 10^{-3}$ mole $l.^{-1}$ AIBN at 60°C in the presence of cupric chloride with methyl cyanide as solvent.

Curves a, b, c and d refer to $CuCl_2$ concentrations of 4, 6, 8 and 10×10^{-4} mole $l.^{-1}$ respectively.



yellow colour of the cupric species in solution faded during the inhibition reaction and had completely disappeared by the end of the induction period. Secondly, the reactions at initial cupric chloride concentrations greater than 6×10^{-4} mole $l.^{-1}$ (approximately), represented by curves (c) and (d) in fig. 35. In these reactions, a dark precipitate appeared at the beginning of the inhibition reaction. This appeared to become colourless during the polymerisation following the induction period. The rate of polymerisation was retarded and continuously changing.

These complex reactions were not examined more fully in this present study, but they indicate the effect of possible complex ion formation, which has been found in cupric chloride-methyl cyanide solutions, on the polymerisation reaction.

SECTION 3 - SPECTROPHOTOMETRIC MEASUREMENTS

The fundamental equation which relates the incident and transmitted radiation for the absorption of light by a substance in solution is known as Beer's Law, one form of which is ,

$$\log Io/I = \epsilon ct,$$

where ϵ, c and t are the extinction coefficient, the concentration of solution and the thickness of absorbing medium respectively. Log Io/I is the logarithmic ratio of the intensity of the incident light to that of the emergent light and is known as the optical density (or absorbance).

Thus, for solutions obeying Beer's Law, the optical density is proportional to the concentration, and by observing the change in optical density, the change of concentration of the substance in solution may be measured.

RATE OF REMOVAL OF CUPRIC CHLORIDE IN DMF SOLUTION IN THE ABSENCE OF MONOMER.

The optical density measurements were made in the visible region of the spectrum at $60^{\circ}C$.

Fig. 36 shows the absorption spectra for cupric chloride concentration from 0·8 to 5·4 x 10^{-3} mole $l.^{-1}$. The plot of optical density, measured at the absorption peak at 436 mμ, against cupric chloride concentration is shown in fig. 37; it is linear in agreement with Beer's Law. The spectra measured during the reaction is shown in fig. 38 and the

Fig.36 Absorption spectra for cupric chloride in DMF.

$[CuCl_2]$ = 0·8 - 5·4 x 10^{-3} mole $l.^{-1}$ for spectra a - g.

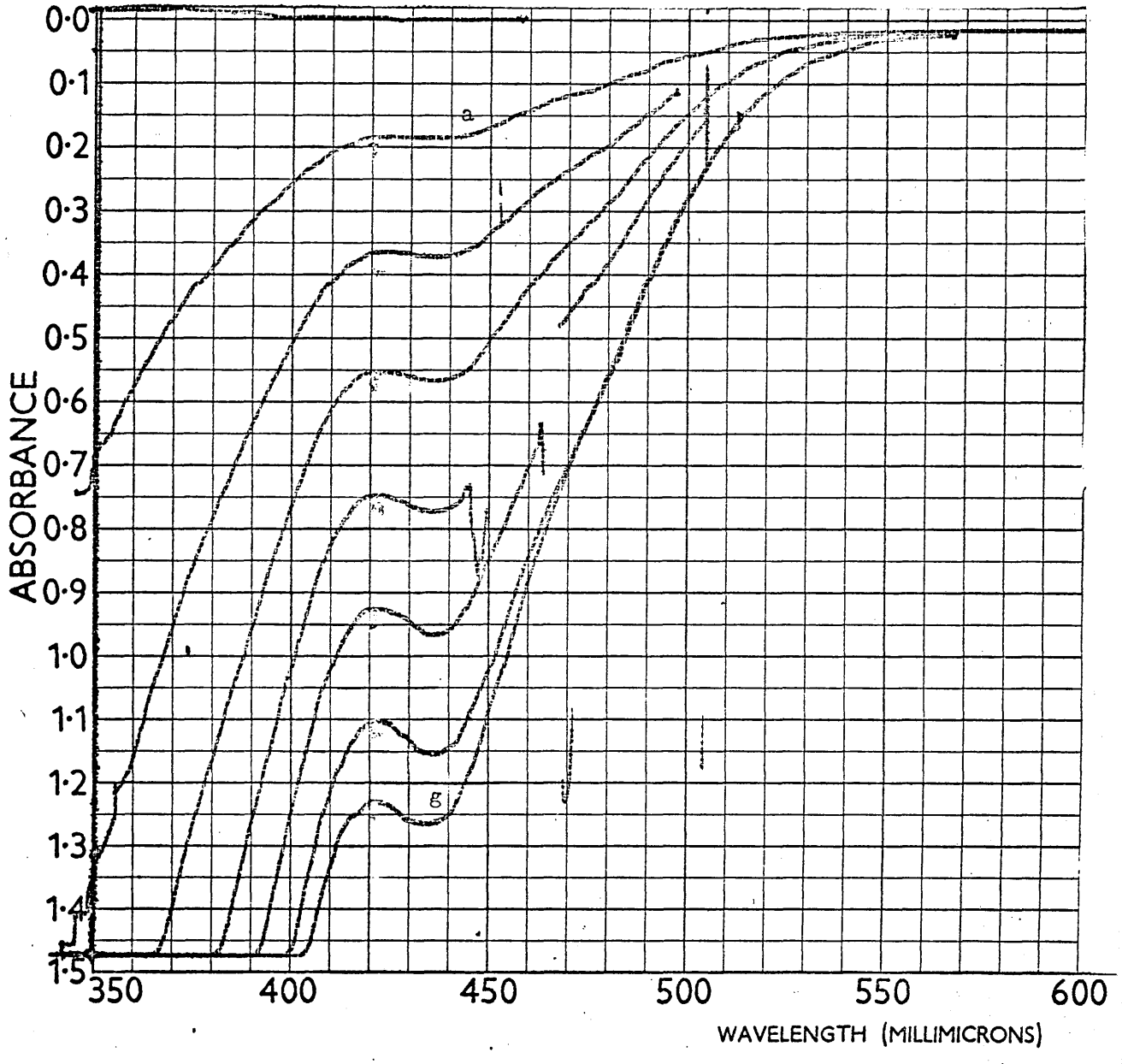


Fig.37 Optical density (4360Å) against cupric chloride concentration in DMF

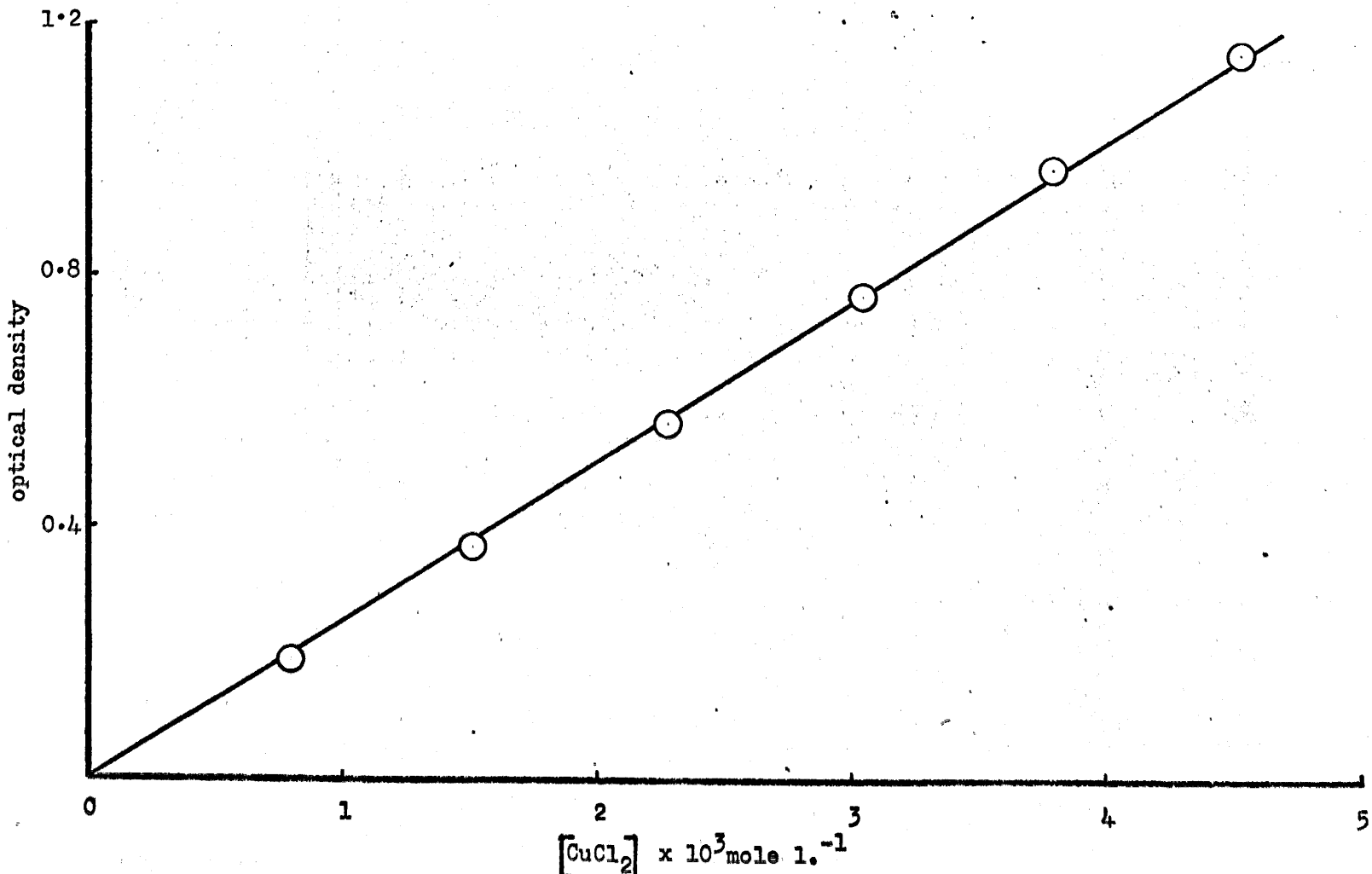
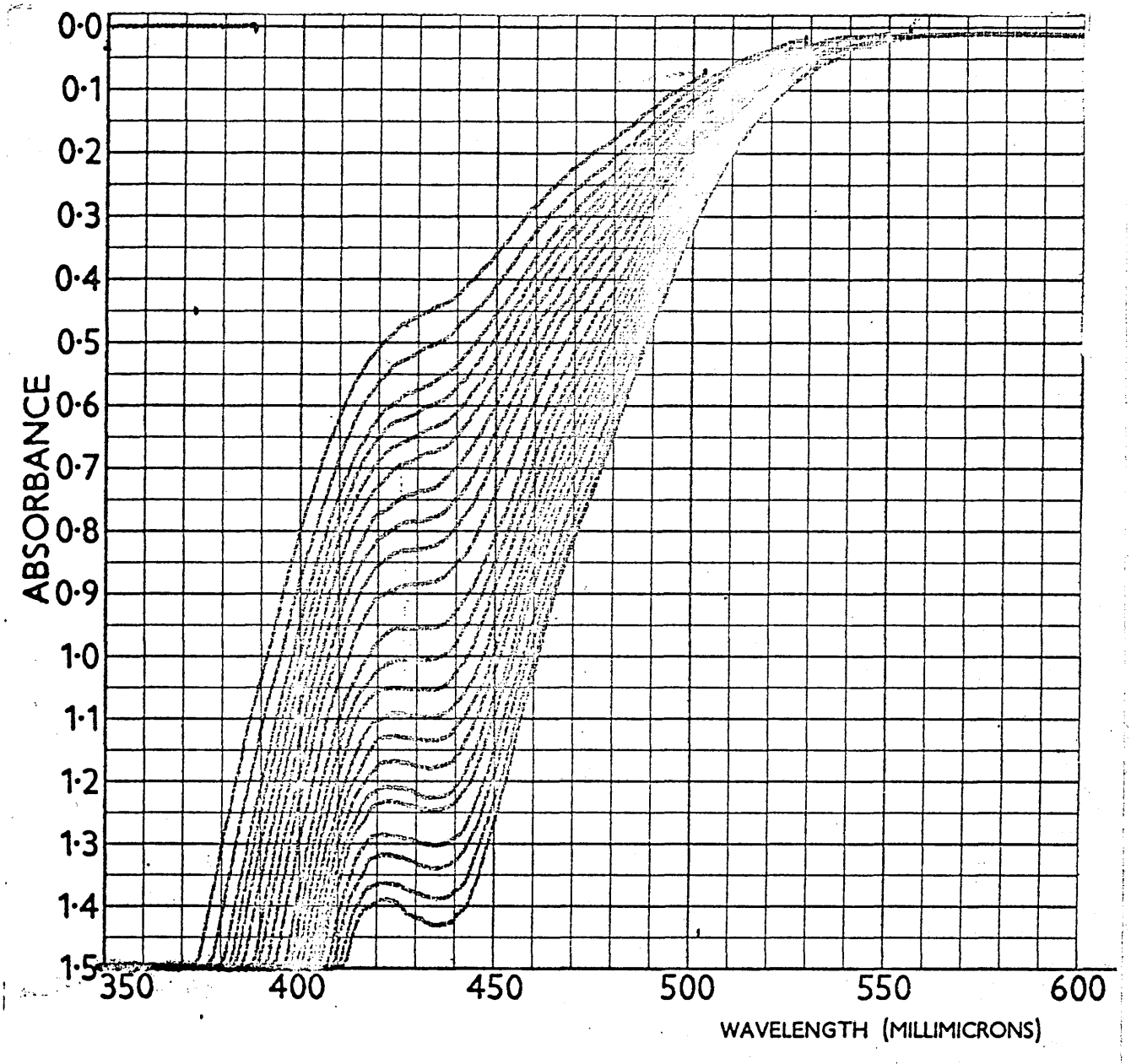


Fig.38 Change of optical density with time for cupric chloride in DMF.

$[AIBN] = 2{\cdot}5 \times 10^{-2}$ $[CuCl_2]_o = 5{\cdot}5 \times 10^{-3}$ mole $l.^{-1}$



initial rate of removal of cupric chloride is illustrated in fig. 39 for an initial AIBN concentration of $7{\cdot}5 \times 10^{-2}$ mole $l.^{-1}$. The results measured at different initial catalyst concentrations are summarised in Table 10.

Table 10. - Rate of removal of cupric chloride in DMF solution at various AIBN concentrations.

$-d[CuCl_2]/dt$ (mole $l.^{-1}$ sec^{-1})	$[AIBN]$ (mole $l.^{-1}$)	$-d[CuCl_2]/dt / [AIBN]$ (sec^{-1})
$7{\cdot}33 \times 10^{-7}$	$2{\cdot}5 \times 10^{-2}$	$2{\cdot}93 \times 10^{-5}$
$10{\cdot}44 \times 10^{-7}$	$5{\cdot}0 \times 10^{-2}$	$2{\cdot}09 \times 10^{-5}$
$14{\cdot}0 \times 10^{-7}$	$7{\cdot}5 \times 10^{-2}$	$1{\cdot}87 \times 10^{-5}$

RATE OF REMOVAL OF CUPRIC CHLORIDE IN AN/DMF SOLUTION

The optical density measurements were made in the visible region of the spectrum at 60°C, and at a constant ratio of AN/DMF, with $[M] = 12{\cdot}92$ mole $l.^{-1}$. This allows a comparison to be made with the methyl methacrylate system, under similar conditions. The additional of AN gives rise to a new absorption peak at 467 mμ which obeys Beer's Law as illustrated in fig 40. The change of optical density during inhibition is shown in the spectra in fig. 41 and refers to an AIBN concentration of 4×10^{-2} mole $l.^{-1}$. Fig. 42 shows the cupric chloride plotted against time for an AIBN concentration of 5×10^{-2} mole $l.^{-1}$. The initial rate of removal of cupric chloride was measured at three AIBN concentrations, and the results are shown in Table 11. In each case the initial cupric chloride concentration was

Fig.39 Initial removal of cupric chloride in DMF solution

$[AIBN] = 5{\cdot}0 \times 10^{-2}$ mole $l.^{-1}$.

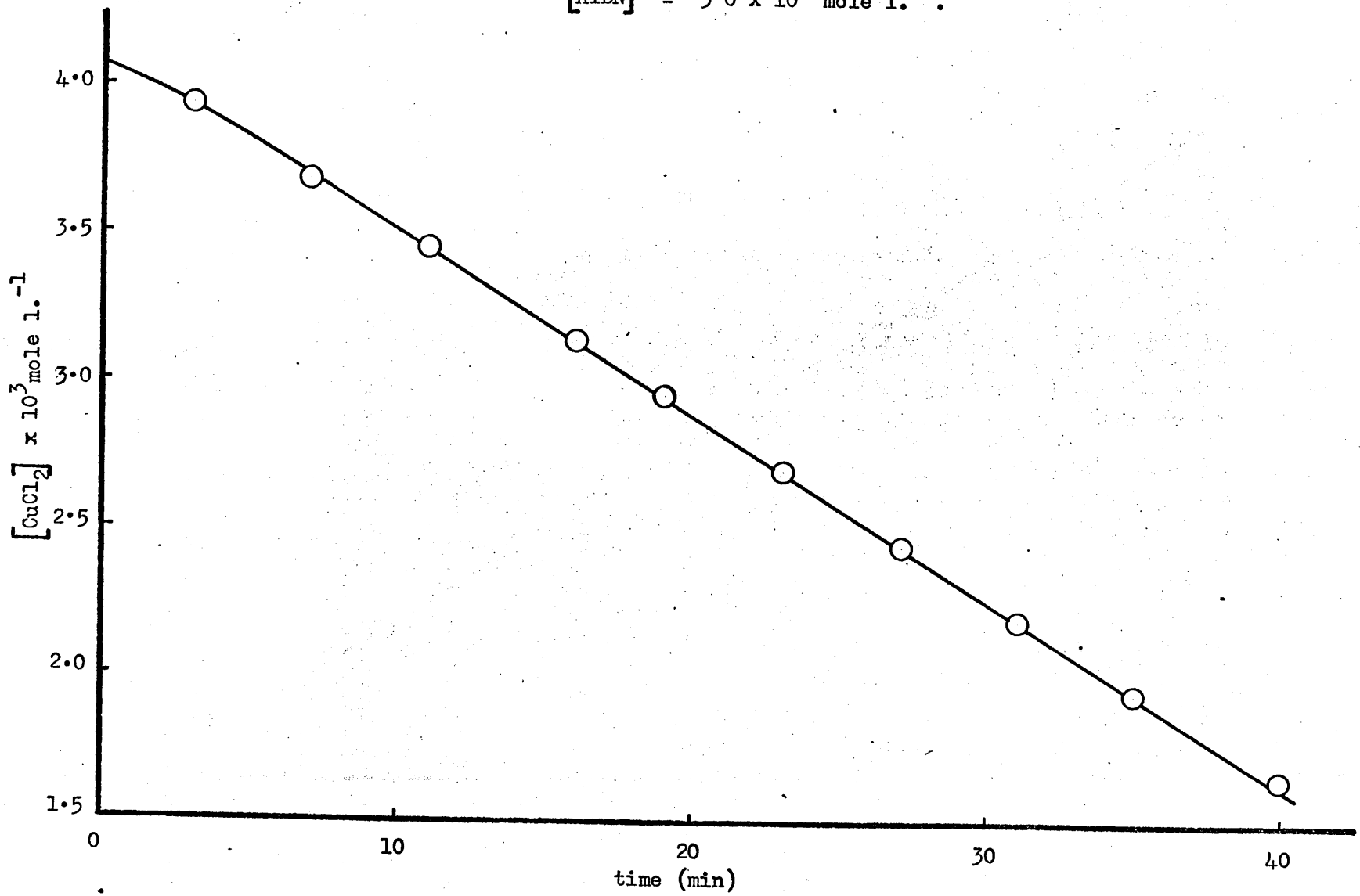


Fig.40 Optical density (4670Å) against cupric chloride concentration in AN/DMF solution.

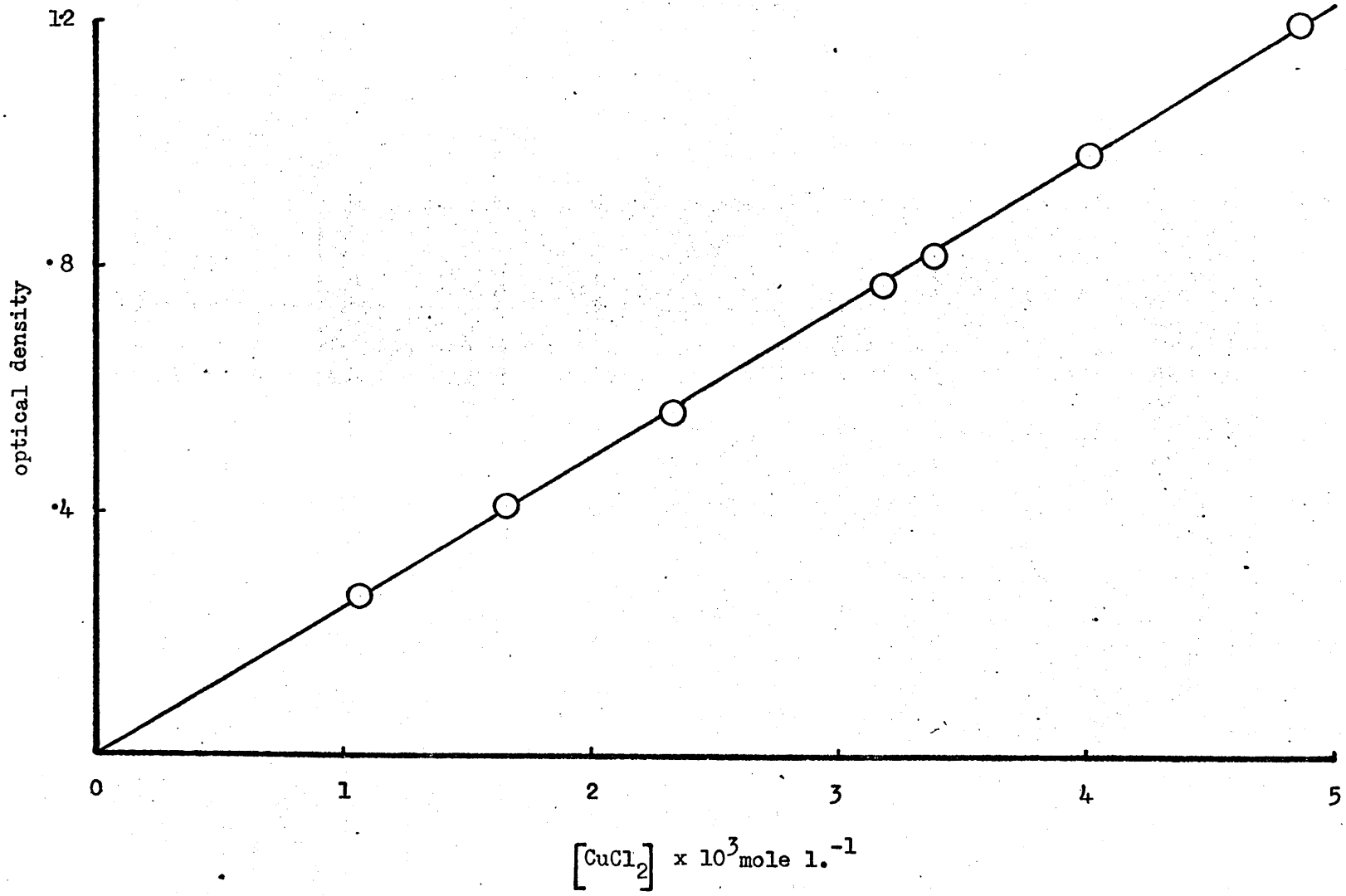


Fig.41 Absorption spectra of cupric chloride in AN/DMF solution measured during inhibition.

$[AIBN] = 4 \times 10^{-2}$ mole $l.^{-1}$. $[CuCl_2]_o = 4.87 \times 10^{-3}$ mole $l.^{-1}$.

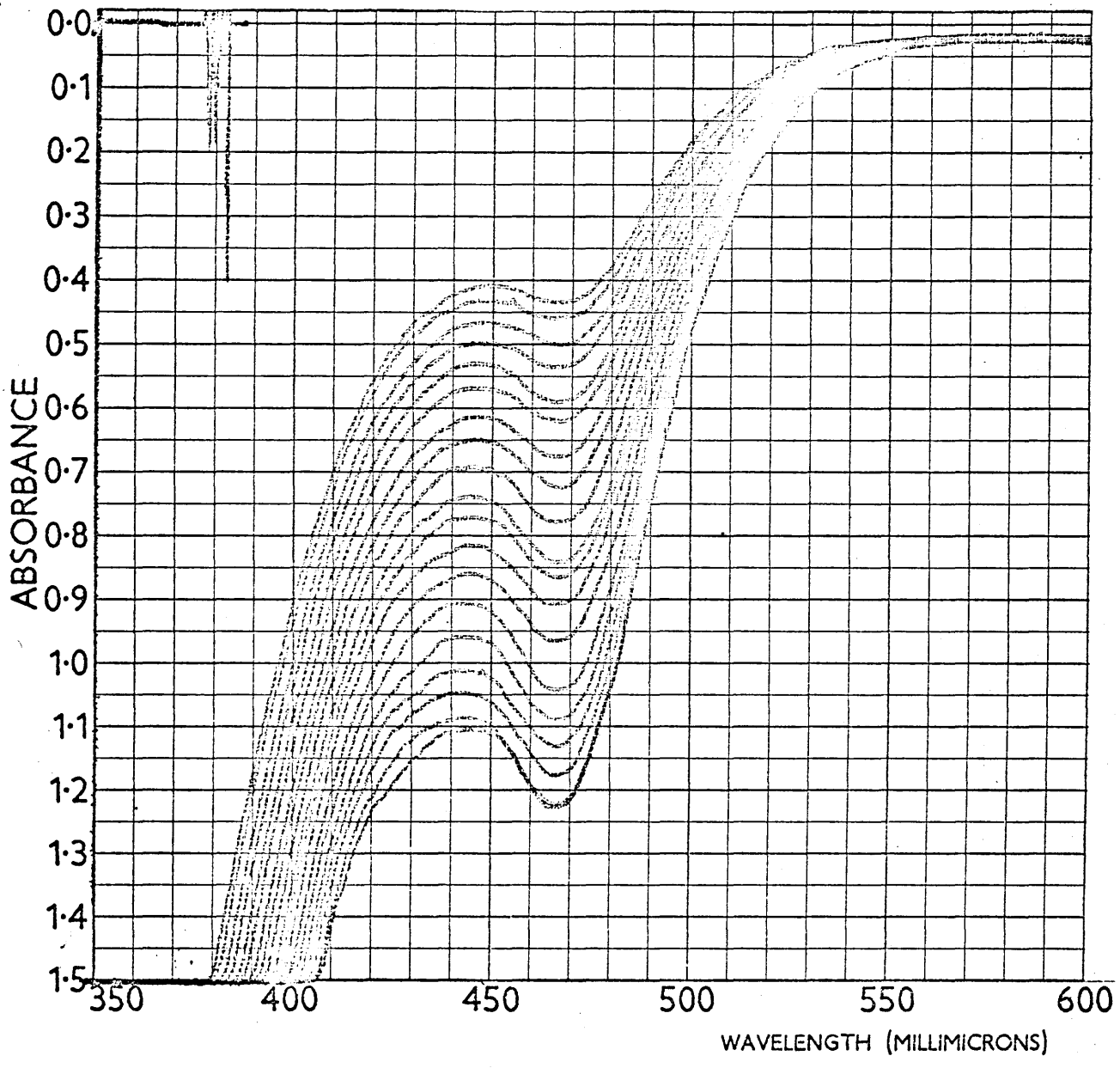
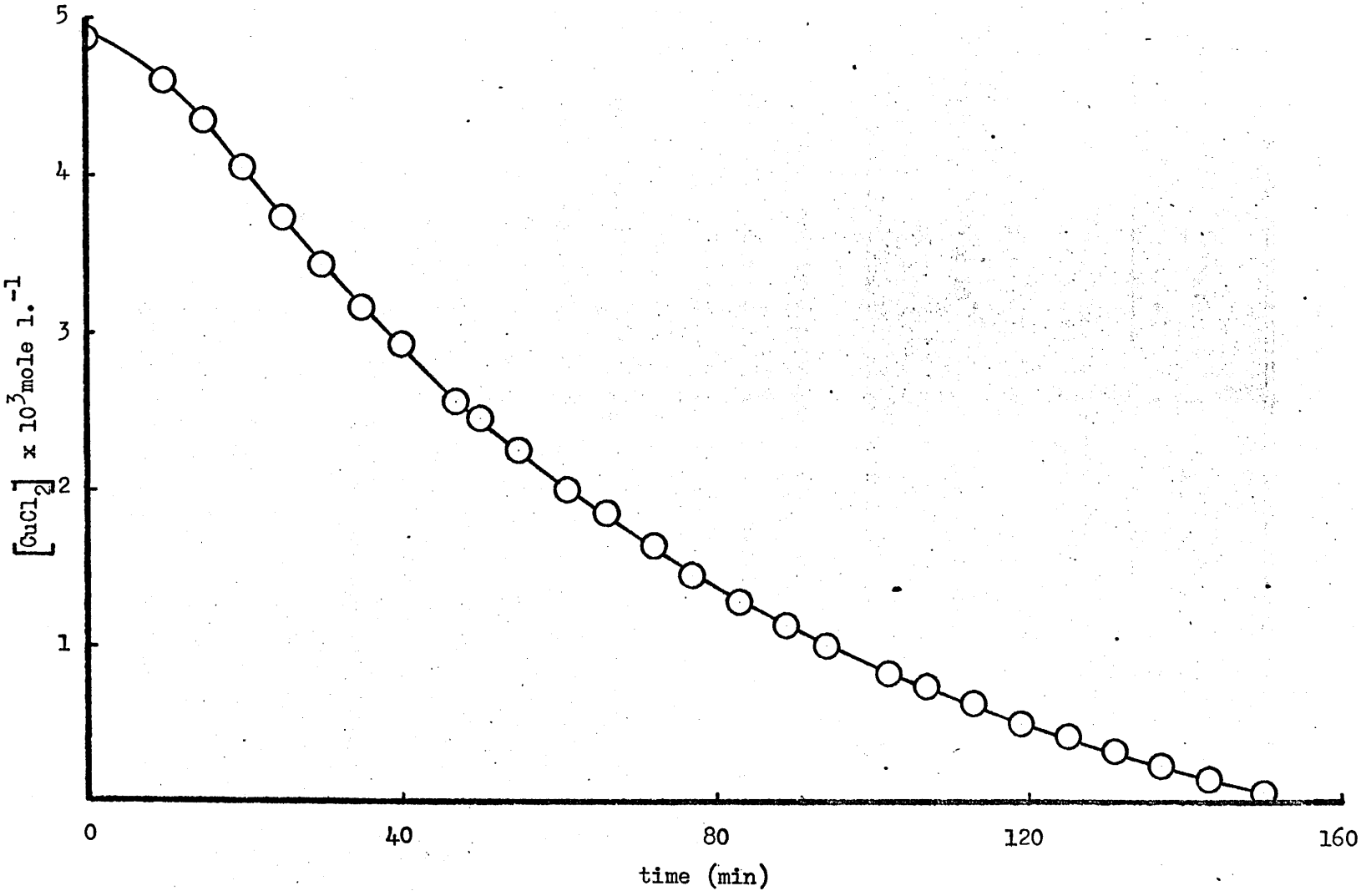


Fig.42 Removal of cupric chloride during the inhibition of the polymerisation of AN.

$[AIBN] = 5 \times 10^{-2}$ mole $l.^{-1}$.



$4{\cdot}87 \times 10^{-3}$ mole $l.^{-1}$.

Table 11 - Rate of removal of cupric chloride in AN/DMF solution at various AIBN concentrations.

$-d[CuCl_2]/dt$ (mole $l.^{-1} sec^{-1}$)	$[AIBN]$ (mole $l.^{-1}$)	$-d[CuCl_2]/dt / [AIBN]$ (sec^{-1})
$6{\cdot}7 \times 10^{-7}$	$4{\cdot}0 \times 10^{-2}$	$1{\cdot}68 \times 10^{-5}$
$8{\cdot}7 \times 10^{-7}$	$5{\cdot}0 \times 10^{-2}$	$1{\cdot}74 \times 10^{-5}$
$10{\cdot}3 \times 10^{-7}$	$6{\cdot}0 \times 10^{-2}$	$1{\cdot}70 \times 10^{-5}$

RATE OF REMOVAL OF CUPRIC CHLORIDE IN MM/DMF SOLUTION

The optical density measurements were made at 60°C with constant $[M]$ = 8·06 mole $l.^{-1}$ as in the dilatometric determination of the inhibition periods.

The spectrum obtained when MM is added to the $CuCl_2$/DMF system is shown in fig. 43 for cupric chloride concentrations from $2{\cdot}16 \times 10^{-3}$ mole $l.^{-1}$ to $10{\cdot}7 \times 10^{-3}$ mole $l.^{-1}$. As with the AN/DMF system, a new peak is formed at 467 mμ. The peak in the MM system is much less distinct than that obtained with AN/DMF. Thus all measurements used in determining the rate of removal of cupric chloride were made at optical densities above 0·5 where the optical density is a lineal function of cupric chloride concentration as shown in fig. 44. The initial rate of removal of cupric chloride is illustrated in fig. 45 for an AIBN concentration of $5\ 0 \times 10^{-2}$ mole $l.^{-1}$. The rate of removal of cupric chloride was measured at three AIBN concentrations and the results are shown in Table 12.

Fig.43 Absorption spectra for cupric chloride in MM/DMF solution.

$[CuCl_2]$ = 2·16 - 10·7 x 10^{-3} mole $l.^{-1}$ for spectra a - f.

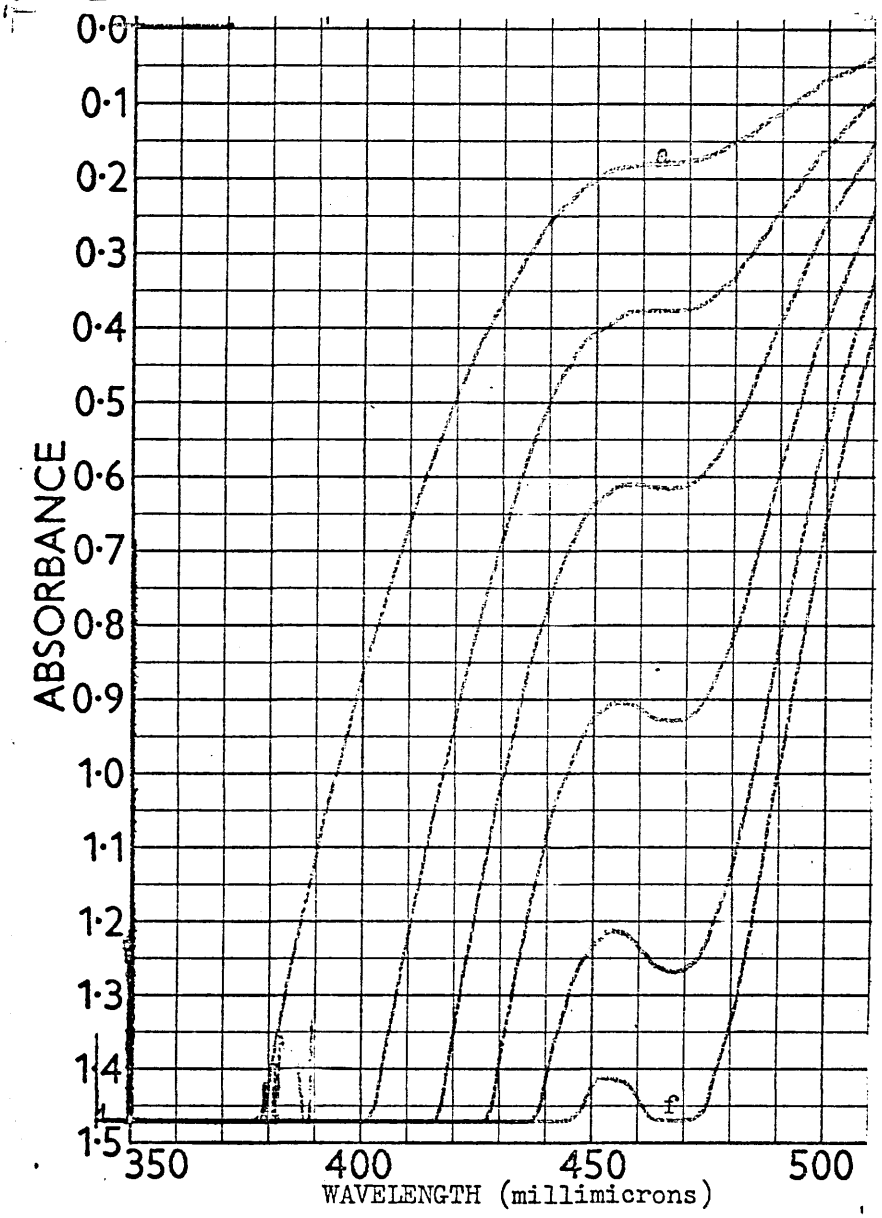


Fig.44 Optical density (4670Å) against cupric chloride concentration in MM/DMF solution.

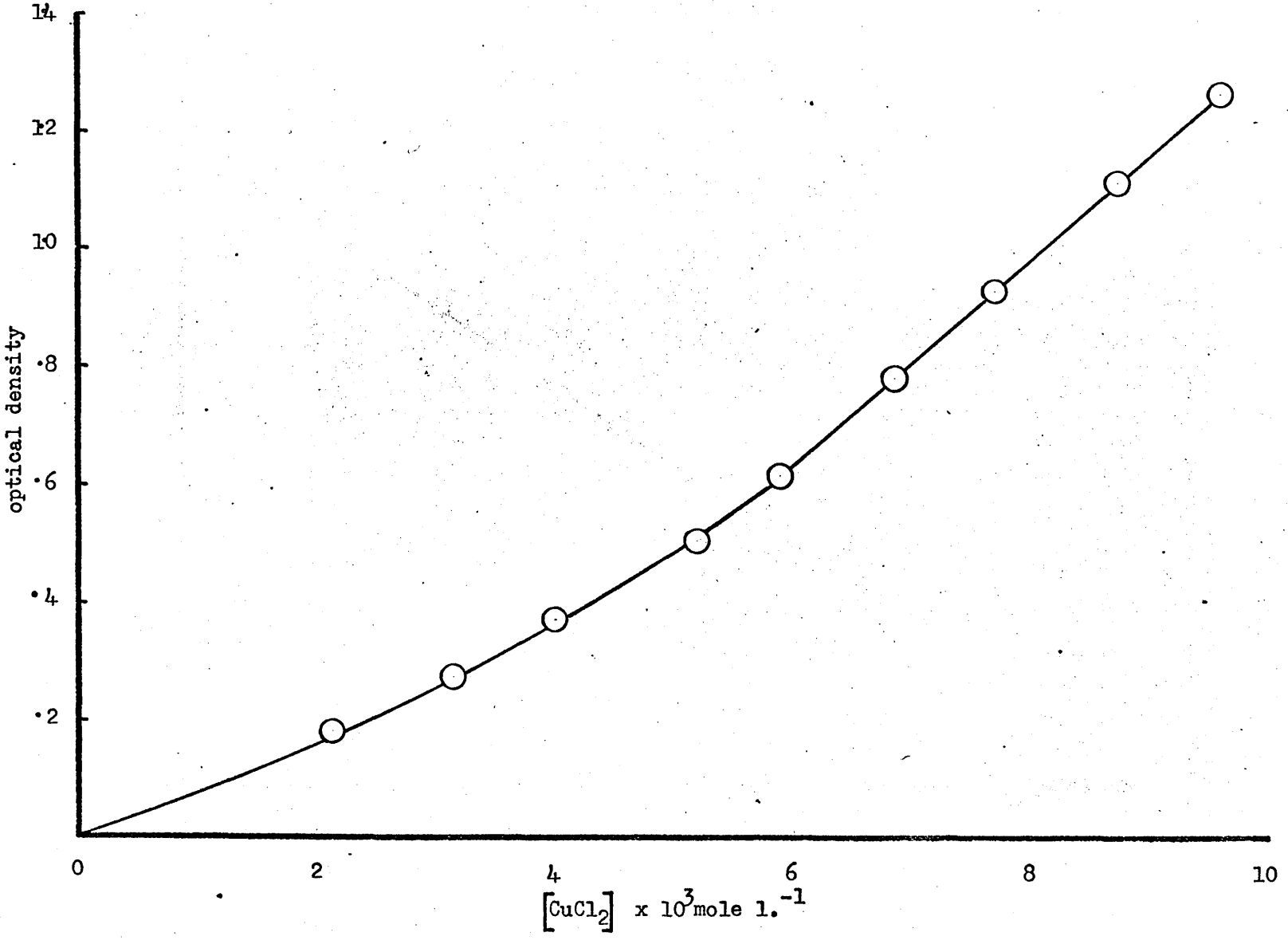


Fig.45 Initial removal of cupric chloride during the inhibition of the polymerisation of MM.

$[AIBN] = 5 \times 10^{-2}$ mole $l.^{-1}$.

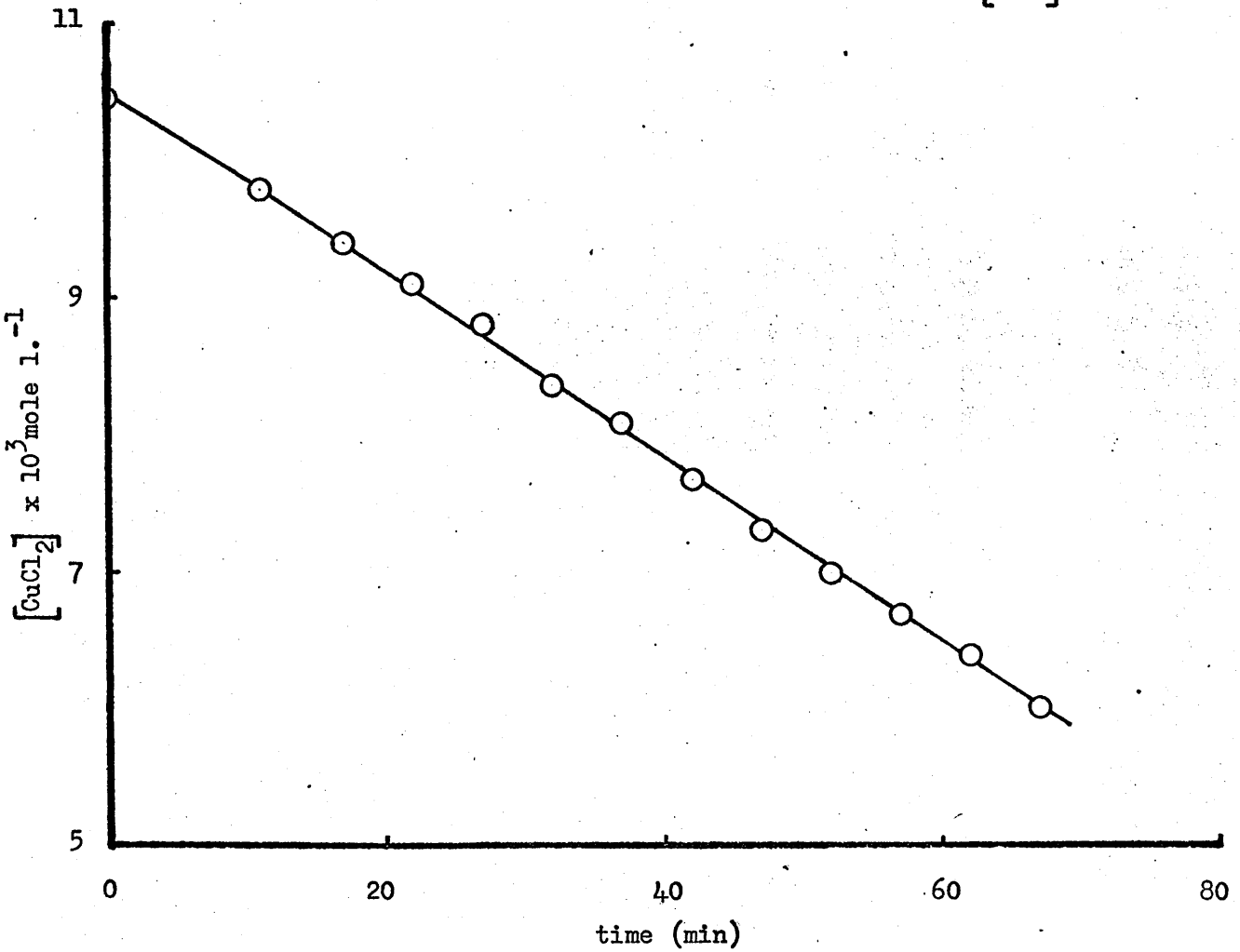


Table 12 - Rate of removal of cupric chloride in MK/DMF solution at various AIBN concentrations.

$-d[CuCl_2]/dt$ (mole $l.^{-1} sec^{-1}$)	$[AIBN]$ (mole $l.^{-1}$)	$-d[CuCl_2]/dt / [AIBN]$ (sec^{-1})
$1{\cdot}11 \times 10^{-6}$	$5{\cdot}0 \times 10^{-2}$	$2{\cdot}22 \times 10^{-5}$
$1{\cdot}44 \times 10^{-6}$	$7{\cdot}5 \times 10^{-2}$	$1{\cdot}92 \times 10^{-5}$
$1{\cdot}91 \times 10^{-6}$	$1{\cdot}0 \times 10^{-1}$	$1{\cdot}91 \times 10^{-5}$

THE ABSORPTION SPECTRUM OF $CuCl_2$ IN ACETONITRILE.

Fig. 46 shows the absorption spectrum of cupric chloride in acetonitrile in the visible region of the spectrum, where a clear absorption peak at 464 mμ is obtained. Fig. 47 refers to a plot of the optical density, measured at 464 mμ against cupric chloride concentration. It is linear in agreement with Beer's Law.

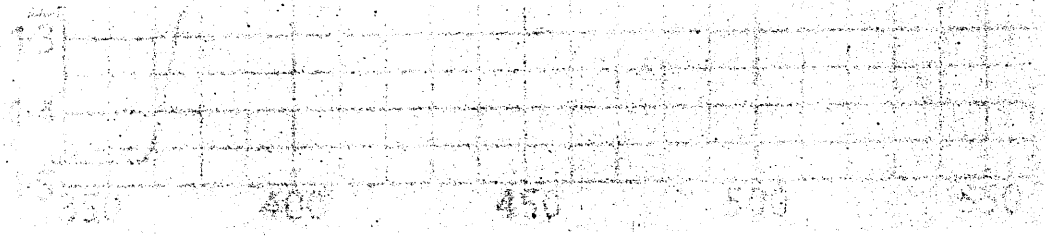


Fig.46 - Absorption spectrum of cupric chloride in methyl cyanide.

$[CuCl_2] = 1{\cdot}24 \times 10^{-3}$ mole $l.^{-1}$.

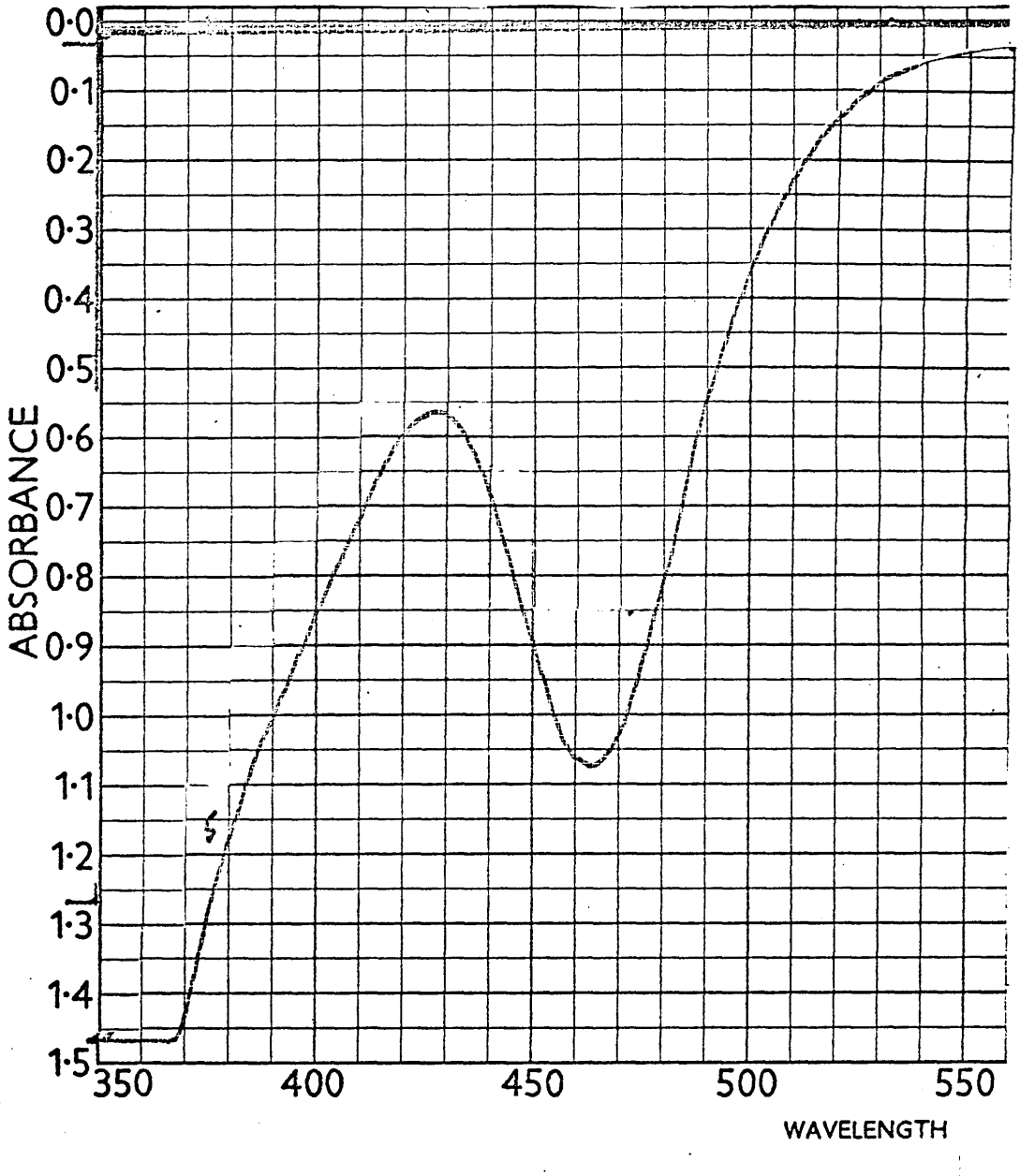
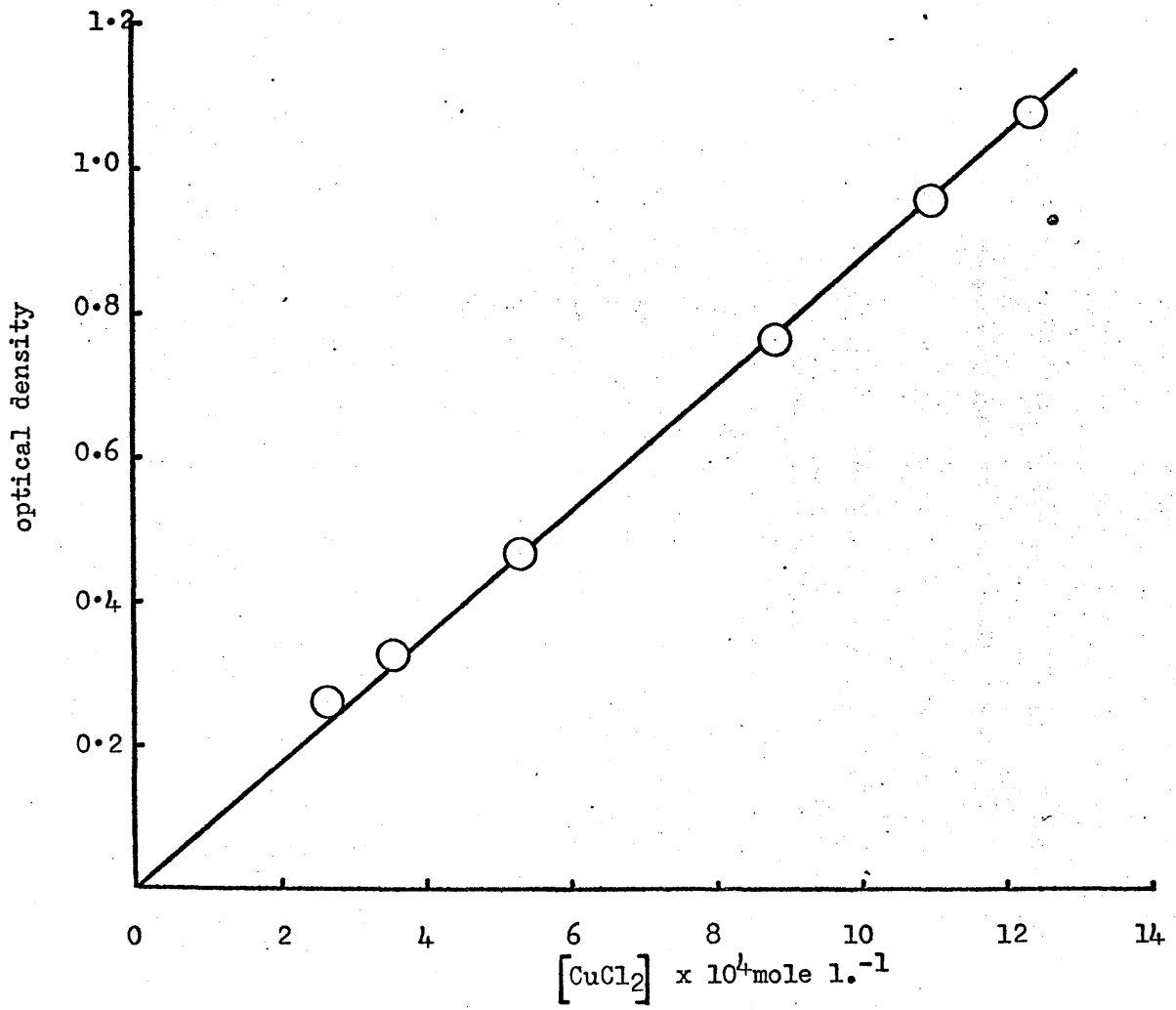


Fig.47 - Optical density (4640Å) against cupric chloride concentration in methyl cyanide solution.



DISCUSSION

The inhibition and retardation reactions involving the oxidation of polymer radicals by metal salts are influenced by many variables. These factors include the charge distribution and steric properties of the substituent groups on the radical, the metal and the metal salt anion, the solvent system and complex formations within the system. Before considering some of these effects with respect to the mechanism, it is necessary to consider possible complex formations.

No extensive studies were carried out to isolate or identify possible copper salt complexes with solvent and/or monomer in the systems but their existence is indicated by the spectrophotometric results. Katzin[42] assigns the peak at 438 mμ in the spectrum of $CuCl_2$ in DMF to the tetrahedral ion $[CuCl_3.DMF]^-$. It is suggested that the absorption peak arises from electron transfer from the metal ion to the ligand, the normal electron transfer peaks for movement from chloride to the metal ion occurring further in the ultra violet[43].

The formation of the new peak at 468 mμ when AN is added to the $CuCl_2$/DMF system is probably due to the formation of a $CuCl_2$ - AN complex. Kern[44] has examined and characterised a range of complexes of AN with metal halides in the transition

series. With cupric chloride a complex of empirical formula $CuCl_2(AN)_{0.5}$ was obtained. These results have been confirmed more recently by Bengough and Jamieson[45] who isolated the complex and confirm that the bonding between the metal and acrylonitrile involves donation of electrons from the nitrogen atom to the metal ion. From a further spectrophotometric study they assign the absorption peak at 468 mμ in the AN/DMF system to the replacement of the DMF by AN in the tetrahedral ion, i.e. $[CuCl_3.AN]^-$. Any complex association of $CuCl_2$ with methyl methacrylate would seem doubtful since $CuCl_2$ is almost completely insoluble in MMA. The second peak formed when MMA is added to the $CuCl_2$/DMF system is possibly due to a second chloro-cupric complex with DMF.

In the cupric chloride inhibited polymerisation of acrylonitrile the corrected value of the rate constant for the initiation reaction ($2k_i$) obtained from the inhibition against time plot is $1{\cdot}51 \times 10^{-5} sec^{-1}$. This value is considerably higher than the value, $1{\cdot}38 \times 10^{-5} sec^{-1}$, for the corresponding methyl methacrylate inhibition and the value, $1{\cdot}40 \times 10^{-5} sec^{-1}$, for the cupric bromide inhibited polymerisation of methyl methacrylate. The values for the rate constants for initiation in the methyl methacrylate system lie within the range $1{\cdot}33 - 1{\cdot}44 \times 10^{-5} sec^{-1}$ found by Bamford et al.[4] for methyl acrylate, methyl methacrylate, methacrylonitrile and acrylonitrile using ferric chloride as inhibitor. The value obtained in the acrylonitrile system is considerably higher than this range of values but lower than the earlier value of $1{\cdot}87 \times 10^{-5} sec^{-1}$ obtained by Bamford et al.[2] for the polymerisation of AN in DMF solution.

The difference in rates of initiation in the two systems may be due in part to differences in the rate of decomposition of AIBN in the different solvent systems - 10% by volume DMF in the MM system and 80% by volume DMF in the AN system. The work of Betts, Dainton and Ivin[26], however, indicates that the decomposition of AIBN is slower in DMF than in most other solvents. Another possibility is that the efficiency of scavenging is less in the AN - DMF system than in the MM - DMF system. This is possible if different complex species exist in these systems[45] and not all the complex species formed are efficient scavengers forthe poly-acrylonitrile radicals. The inactivity of certain cupric forms is illustrated by the inactivity of cupric acetate and cupric nitrate in the AIBN initiated polymerisation of methyl methacrylate. Also the increased rates of initiation obtained when small quantities of water are added to the $CuCl_2$ inhibited polymerisation of methyl methacrylate and when acetonitrile is used as solvent suggest the existence of inefficient scavengers.

The value of 32·9 kcal/mole for the energy of activation for initiation obtained from the plot of log $2k_i$ against $1/T^{o}K$ for the cupric chloride and cupric bromide inhibited polymerisation of methyl methacrylate is close to the value for Ed, the activation energy for the decomposition of AIBN into free radicals, indicating that this is probably the rate controlling step in the initiation process.

With the acrylonitrile inhibited polymerisation the experimental studies were completed before the suitable kinetic analysis was derived for solving the rate constant ratio k_y/k_p and k_x/k_p. Thus only the reactions carried out within the limits of the function

would be desired for the measurement of ϕ', the plots of the function of ϕ' were restricted to values where there was a minimum variation in the function with changes in ϕ'. This was $0{\cdot}4 < \phi' < 0{\cdot}8$ for derivations using equation (46) and $0{\cdot}25 < \phi' < 0{\cdot}8$ for derivations using equation (57) as illustrated in fig. 8 and fig. 10 respectively. The higher values of the ratio k_x/k_p obtained in the latter-type plots are obviously due to the effects of points at low ϕ' on the gradients of the lines.

With the methyl methacrylate systems the experiments and experimental techniques were designed to suit the calculations and wider values of ϕ_t were used in the derivations.

The deviations from linearity obtained, particularly at low values of ϕ_t and ϕ' may be mainly due to the difficulty in measuring the gradients accurately at low conversions. On the other hand it may reflect a thermal effect which was very obvious in the cupric bromide reaction using the normal unmodified dilatometer. The temperature rise inside the dilatometer at the onset of polymerisation would cause the greater distortion during the early stages of the reaction, i.e. at low ϕ values, until thermal equilibrium is regained. There were no indications of thermal instability in the dilatometric studies but measurement of temperature changes within the dilatometer would be required to verify this possibility.

The values for the rate constants for the reaction between cupric chloride and polyacrylonitrile radicals and cupric chloride and cupric bromide with polymethyl methacrylate

radicals are of a higher order than those obtained by Bamford et al [4] for the reaction between these polymer radicals with $FeCl_3$ (by a factor of 45 with AN and a factor 252 with MM). Thus the cupric salt appears to be a much more effective radical trap than the corresponding ferric salt.

The greater reactivity of the cupric bromide over cupric chloride towards polymethyl methacrylate radicals (approximately a factor of 2 in rate constant) is in the same order of reactivity as found by Entwhistle [28] for the ferric halides; whereas ferric bromide inhibits the polymerisation of methyl methacrylate, ferric chloride merely retards it. The difference in reactivity of the bromide and chloride may tentatively be attributed to the importance of the oxidation/reduction potential of the salt, although the importance of such factors as atom and bond polarisabilities and bond strengths cannot be overlooked.

Thus the order of reactivity of the salts to polymethyl methacrylate radicals may be written as

$$CuBr_2 > CuCl_2 > FeCl_3 \quad \text{and} \quad FeBr_2 > FeCl_3 \ ,$$

and the rate constants for the cupric salt reactions are of the order found for the reaction of the free radical DPPH with polymethyl methacrylate radicals measured using a similar technique to those used in this study [46].

Bamford et al have evaluated the rate constants for the reactions of ferric chloride with a number of polymer

radicals and compared the values obtained with the general reactivities of the radicals. The experimental measure used for the general reactivity was the velocity coefficient, k_{TR}, of chain transfer to toluene at 60°C. These values are shown in the following table with the results obtained for the $CuCl_2$ reactions.

Table 13 - Comparison of k_x values at 60°C for the polymerisation of methyl methacrylate acrylonitrile, methacrylonitrile and styrene in the presence of ferric chloride and cupric chloride and comparison with k_{TR} values.

Polymer Radical	$k_x(FeCl_3)$ $(mol^{-1}l.sec^{-1})$	k_{TR} $(mol^{-1}l.sec^{-1})$	$k_x(CuCl_2)$ $(mol^{-1}l.sec^{-1})$
Vinyl Acetate	$2{\cdot}35 \times 10^{6}$	$7{\cdot}73$	
Styrene	$5{\cdot}4 \times 10^{4}$	$2{\cdot}11 \times 10^{-3}$	$1{\cdot}76 \times 10^{6}$ (47)
Acrylonitrile	$4{\cdot}5 \times 10^{3}$	$7{\cdot}85 \times 10^{-1}$	$1{\cdot}9 \times 10^{5}$
Methyl Acrylate	$4{\cdot}15 \times 10^{3}$	$5{\cdot}6 \times 10^{-1}$	
Methyl Methacrylate	$3{\cdot}05 \times 10^{3}$	$1{\cdot}25 \times 10^{-2}$	$7{\cdot}7 \times 10^{5}$
Methacrylonitrile	$3{\cdot}15 \times 10^{2}$	2×10^{-2}	9×10^{5} (48)

As with the ferric chloride reactions, the rate constants for the cupric chloride reactions are not in agreement with the general reactivity of the polymer radicals. There is, however, a difference in the sequence of radical reactivity toward ferric chloride and cupric chloride.

It has been well established that the oxidation of

free radicals by metal salts proceeds by at least two mechanisms, electron transfer and ligand transfer. In the transition state of an electron transfer mechanism oxidation is accompanied by the development of a positive charge on the carbon moiety, whereas the requirements for the ligand transfer process are more akin to atom transfer reactions of free radicals. It has been suggested that even in the ligand transfer oxidation there is a modicum of positive charge generated in the free radical moiety.

The electron transfer mechanism proceeds through a cationic transition state, e.g.

$$R^{\bullet} + Cu^{2+}X \rightarrow \left[R^{\bullet}XCu^{2+} \longleftrightarrow R^{+}XCu^{+}\right] \rightarrow Cu^{+} + \text{Carbonium products.}$$

In the ligand transfer mechanism the transfer of an atom or radical from the metal oxidant to the carbon radical moderates the development of charge in the transition state, e.g.

$$R^{\bullet} + Cu^{2+}X \rightarrow \left[R^{\bullet}X{-}Cu^{2+} \longleftrightarrow R{-}XCu^{+}\right] \rightarrow R{-}X + Cu^{+} ,$$

and this mechanism is analogous to the bridged activated complex described by Taube [22] for the completely inorganic system mentioned earlier.

Bamford favours the electron transfer mechanism, the net positive charge on the carbon atom carrying the unpaired electron explaining the lower rate constants obtained with radicals with electron withdrawing substituents, which will react less readily than would be expected from their general reactivity.

Kochi and co-workers [49,50,51,52] have made an extensive study of the oxidation of alkyl radicals by metal salts, in both aqueous and non aqueous solutions. They interpret the oxidation of the radical by copper salts with reference to the electronic structure of the radical and copper salt anion. In the telemorisation reactions of various vinyl monomers with 5 - (methoxycarbonyl) pentyl radical in the presence of metal salts, e.g.

$$CH_3O_2C(CH_2)_4\dot{C}H_2 + CH_2 = CHX \longrightarrow CH_3O_2C(CH_2)_6\cdot CHX$$

$$\downarrow +MY_n$$

products

it was found that when X was an electron withdrawing group such as halogen, carbonyl or cyano, oxidation of the adduct radical by electron transfer oxidants such as cupric acetate and perchlorate was slow, but rapid with ligand transfer reagents such as cupric and ferric chloride.

Minisci and Galli [53] reported conflicting results which indicated that the oxidation was independent of the anion, with cupric acetate, sulphate and nitrate being suitable oxidants in the following reaction.

$$HO_2C(CH_2)_6\dot{C}HCN + Cu^{2+} \longrightarrow HO_2C(CH_2)_6\overset{+}{C}HCN + Cu^{+}$$

$$HO_2C(CH_2)_6\overset{+}{C}HCN + H_2O \longrightarrow HO_2C(CH_2)_6CH(OH)CN$$

$$HO_2C(CH_2)_6CH(OH)CN \longrightarrow HO_2C(CH_2)_6CHO \text{ etc.}$$

The observed rapid oxidation of the polymethyl

methacrylate radical by cupric chloride and cupric bromide and the inertness of this radical with respect to oxidation by cupric acetate and cupric nitrate support the results of Kochi, and indicate a ligand transfer mechanism for the oxidation of polymethyl methacrylate radicals by cupric chloride and cupric bromide.

The changes in solvent significantly affects the oxidation reaction. The addition of small quantities of water to the $CuCl_2$/MM/DMF system causes a reduction in the rate constant of the oxidation reaction. This may be due to the stabilisation of the cupric ion as the aquo species [54] which makes it a less potent oxidant, and a concomitant destablisation of the cuprous salt. In addition, water promotes dissociation of the complex chlorocupric species ($CuCl_n^{+2-n}$) into the lower aquochlorocupric species [30], which may be less effective as ligand transfer oxidants.

Very little may be concluded about the reactions studies using acetonitrile as solvent; but the differences obtained at different $CuCl_2$ concentrations probably reflects a system of $CuCl_2$/MeCN complexes. The induction periods obtained using acetonitrile as solvent are considerably lower than those obtained at the same $CuCl_2$ concentrations using DMF as solvent. This is probably due to the change in the Cu^+/Cu^{2+} oxidation potential brought about by the stabilisation of the cuprous species by acetonitrile [55].

It has become apparent in these studies that complexes of the metal salts with solvent and/or monomer plays a

significant part in the mechanism of the oxidation reactions.

George et al [56,57] have identified a series of complexes in the $FeCl_3$/DMF system and have recently calculated the rate constants at 60°C for polystyryl radicals towards $Fe(DMF)_6^{3+}$, $Fe(DMF)_5Cl^{2+}$, $Fe(DMF)_4Cl_3^{+}$, and $FeCl_4^{-}$ ions to be 847, $4{\cdot}15 \times 10^4$, $6{\cdot}55 \times 10^4$ and $3{\cdot}14 \times 10^4$ $l.mole^{-1}sec.^{-1}$ respectively.

Recent results by Bengough and Jamieson [45] suggest that a series of $CuCl_2$ - DMF complexes are involved and are dependent on the concentration of monomer and reaction temperature. The existence of these different species may explain the difference in the sequence of radical reactivity toward ferric chloride and cupric chloride mentioned earlier, as the rate constants were not determined at the same monomer: DMF ratio in the two systems.

The non-linearity in the Arrhenius plot of k_x for the $CuCl_2$/MM/DMF system would also be explained by a series of temperature dependent $CuCl_2$ - DMF complexes.

Further understanding of this system would require an examination of the different cupric complexes present and the effect of these on the oxidation reaction.

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APPENDIX

Experimental Results and Calculations for the Polymerisation of Acrylonitrile in the presence of $CuCl_2$ initiated by AIBN

$[CuCl_2]_o = 2.02 \times 10^{-3}$ mole $l.^{-1}$ $\quad$ $[AIBN] = 4 \times 10^{-2}$ mole $l.^{-1}$

Reaction Time (min.)	% Polymerisation ($F \times 10^2$)
33	0.0
38	0.092
44	0.401
49	0.878
56	1.968
61	3.039
66	4.290
72	5.950
76	7.105
81	8.496
86	9.950
91	11.31
93	11.90

Reduced rates measured from conversion/time plot and calculated functions.

Time	ϕ'	F	$-1/\phi'-2\cdot3\log\{(1/\phi)-1\}$	$\log\{(1/\phi)-1\}$	$\log(1-F)$
42	0.214	0.0027	-5.964	0.5641	$\bar{1}.99883$
44	0.275	0.0041	-4.604	0.4208	$\bar{1}.99821$
46	0.320	0.0057	-3.876	0.3282	$\bar{1}.99752$
48	0.384	0.0076	-3.076	0.2052	$\bar{1}.99668$
50	0.477	0.0101	-2.190	0.0403	$\bar{1}.99562$
52	0.528	0.0129	-1.619	$\bar{1}.9133$	$\bar{1}.99436$
54	0.614	0.0162	-1.163	$\bar{1}.7980$	$\bar{1}.99292$
56	0.696	0.0199	-0.606	$\bar{1}.6395$	$\bar{1}.99127$
58	0.760	0.0240	-0.156	$\bar{1}.4971$	$\bar{1}.98945$
60	0.816	0.0283	0.261	$\bar{1}.3523$	$\bar{1}.98753$

$[CuCl_2]_o = 6{\cdot}55 \times 10^{-3}$ mole $l.^{-1}$ $[AIBN] = 4 \times 10^{-2}$ mole $l.^{-1}$

Reaction Time (min.)	% Polymerisation ($F \times 10^2$)	Reaction Time (min.)	% Polymerisation ($F \times 10^2$)
107	0.0	170	1.445
122	0.0786	173	1.608
123	0.0932	176	1.789
126	0.1371	180	2.030
128	0.1773	184	2.315
132	0.2249	187	2.536
134	0.2687	189	2.680
136	0.3074	191	2.841
138	0.3381	192	2.916
141	0.3965	195	3.165
145	0.4955	198	3.393
150	0.6305	200	3.560
152	0.6890	203	3.815
153	0.7220	208	4.240
156	0.8170	210	4.410
159	0.9410	213	4.670
163	1.111	215	4.850
164	1.157	219	5.203
167	1.296	220	5.285

Reduced rate measurements from conversion/time plot and calculated functions.

Time	Ø'	F	$-1/Ø'-2.3 \log\{(1/Ø')-1\}$	$\log\{(1/Ø')-1\}$	log(1-F)
145	0.248	0.0050	-5.389	0.4814	$\bar{1}$.99782
155	0.350	0.0079	-3.51	0.2739	$\bar{1}$.99655
160	0.443	0.0106	-2.498	0.1017	$\bar{1}$.99538
165	0.483	0.0120	-2.14	0.0298	$\bar{1}$.99476
170	0.537	0.0145	-1.748	$\bar{1}$.9435	$\bar{1}$.99366
175	0.621	0.0173	-1.101	$\bar{1}$.7853	$\bar{1}$.99246
180	0.704	0.0205	-0.616	$\bar{1}$.6425	$\bar{1}$.99096
185	0.755	0.0240	-0.245	$\bar{1}$.5263	$\bar{1}$.98945
195	0.823	0.0316	0.272	$\bar{1}$.3506	$\bar{1}$.98606

Experimental Results and Calculations for the Polymerisation of Methyl Methacrylate in the Presence of $CuCl_2$ Initiated by AIBN.

$[CuCl_2]_o = 6 \times 10^{-4}$ mole $l.^{-1}$ $[AIBN] = 5 \times 10^{-3}$ mole $l.^{-1}$

Time	% Polymerisation	Time	% Polymerisation
78	0.0007	154	0.1017
83	0.0010	155	0.1096
89	0.0013	156	0.1184
95	0.0023	157	0.1312
97	0.0033	158	0.1458
101	0.0033	159	0.1645
104	0.0033	160	0.1899
109	0.0053	161	0.2293
113	0.0076	162	0.290
116	0.0092	163	0.396
120	0.0115	164	0.54
124	0.0171	165	0.696
127	0.0207	165	0.778
130	0.0237	166	0.86
134	0.0309	167	1.03
136	0.0342	168	1.199
138	0.0378	169	1.363
140	0.0421	171	1.701
142	0.0464	172	1.865
144	0.0516	173	2.034
146	0.0595	174	2.198
148	0.0654	175	2.36
150	0.0753	176	2.521
152	0.0861	177	2.689
153	0.0927	178	2.854

Reduced rate measurements from conversion/time plot and calculated functions.

Time	ϕ_t	F	$\log\{(1-\phi_t^2)/\phi_t\}$	$-1/\phi_t + 2{\cdot}3\log(1+\phi_t/1-\phi_t)$	$\log(1-F)$
159	0.129	0.00165	0.8832	-7.658	$\bar{1}.999237$
160	0.185	0.00190	0.7179	-5.245	$\bar{1}.999174$
160.5	0.236	0.00206	0.6024	-4.03	$\bar{1}.999104$
161	0.298	0.00229	0.485	-3.086	$\bar{1}.999000$
161.5	0.374	0.00255	0.3619	-2.334	$\bar{1}.998891$
162	0.473	0.00290	0.2151	-1.668	$\bar{1}.998739$
162.5	0.627	0.00337	$\bar{1}.9869$	-0.957	$\bar{1}.998533$
163	0.804	0.00396	$\bar{1}.6444$	-0.282	$\bar{1}.998276$

$[CuCl_2]_o = 6{\cdot}0 \times 10^{-4}$ mole $l.^{-1}$ $\quad$ $[AIBN] = 2 \times 10^{-2}$ mole $l.^{-1}$

Time	% Polymerisation
22	0.0
25	0.0007
28	0.0035
30	0.0081
32	0.0141
34	0.0253
36	0.0372
37	0.0477
38	0.0607
39	0.0804
40	0.1032
41	0.1411
42	0.2055

Time	% Polymerisation
43	0.344
44	0.592
45	0.894
46	1.21
47	1.538
48	1.859
49	2.185
50	2.515
51	2.84
52	3.161
53	3.481
54	3.802
55	4.122
56	4.44

Reduced rate measurements from conversion/time plot and calculated functions.

Time	ϕ_t	F	$\log\{(1-\phi_t^2)/\phi_t\}$	$-1/\phi_t + 2.3\log(1+\phi_t/1-\phi_t)$	$\log(1-F)$
41	0.121	0.00141	0.9108	-8.158	$\bar{1}.999388$
$41\frac{1}{2}$	0.195	0.00166	0.6931	-4.956	$\bar{1}.999278$
42	0.302	0.00206	0.4786	-3.041	$\bar{1}.999109$
$42\frac{1}{2}$	0.424	0.00265	0.2865	-1.965	$\bar{1}.998848$
43	0.603	0.00344	0.0241	-1.055	$\bar{1}.998503$
$43\frac{1}{2}$	0.784	0.00460	$\bar{1}.6915$	-0.359	$\bar{1}.997998$

$[CuCl_2]_o$ = 1 3 x 10^{-3} mole $l.^{-1}$

Time	% Polymerisation
85	0.0
86	0.0007
88	0.0013
92	0.0010
97	0.0026
101	0.0010
104	0.0029
106	0.0042
108	0.0059
110	0.0062
112	0.0065
115	0.0091
119	0.0114
122	0.0137
125	0.0163
128	0.0196
130	0.0208
133	0.0261
135	0.0284
136	0.0316
137	0.0322
138	0.0342
140	0.0394
141	0.0427
142	0.0456
143	0.0479
144	0.0509
145	0.0538
146	0.0577
147	0.0619

[AIBN] = 1 x 10^{-2} mole $l.^{-1}$

Time	% Polymerisation
148	0.0658
149	0.0704
150	0.0753
151	0.0797
152	0.0848
153	0.0913
154	0.0968
155	0.1038
156	0.1105
157	0.1183
158	0.1289
159	0.1371
160	0.1491
161	0.1639
162	0.1801
163	0.2001
164	0.224
165	0.2589
166	0.311
167	0.4125
168	0.5915
169	0.814
170	1.051
171	1.285
172	1.52
173	1.758
174	1.998
175	2.22
176	2.449
177	2.675
179	3.124

Reduced rate measurements from conversion/time plot and calculated functions.

Time	ϕ_t	F	$\log\{(1-\phi_t^2)/\phi_t\}$	$-1/\phi_t + 2{\cdot}3\log(1+\phi_t/1-\phi_t)$	$\log(1-F)$
164	0.130	0.00224	0.8773	-7.555	$\bar{1}.999026$
165	0.182	0.00259	0.7264	-5.347	$\bar{1}.998873$
$165\frac{1}{2}$	0.225	0.00282	0.6252	-4.245	$\bar{1}.998778$
166	0.294	0.00311	0.4926	-3.14	$\bar{1}.998648$
$166\frac{1}{2}$	0.419	0.00354	0.2947	-2.002	$\bar{1}.998460$
167	0.577	0.00413	0.0630	-1.162	$\bar{1}.998207$
$167\frac{1}{2}$	0.752	0.00491	-0.2382	-0.481	$\bar{1}.997867$
168	0.908	0.00592	-0.7137	0.216	$\bar{1}.997426$

$[CuCl_2]_o = 4.35 \times 10^{-4}$ mole $l.^{-1}$ $[AIBN] = 1 \times 10^{-2}$ mole $l.^{-1}$

Time	% Polymerisation	Time	% Polymerisation
29	0.0	54	0.397
31	0.0007	55	0.0483
32	0.001	56	0.0595
33	0.0020	57	0.0721
34	0.0013	58	0.0923
35	0.0013	59	0.118
36	0.0020	60	0.1993
37	0.0017	61	0.3462
38	0.0023	62	0.584
39	0.0030	63	0.832
40	0.0031	64	1.09
42	0.0056	66	1.598
43	0.0066	67	1.845
44	0.0086	68	2.085
45	0.0099	69	2.325
46	0.0125	70	2.579
47	0.0136	71	2.821
48	0.0149	72	3.059
49	0.0169	73	3.3
50	0.0195	74	3.543
51	0.0225		
52	0.0272		
53	0.0338		

Reduced rate measurements from conversion/time plot and calculated functions.

Time	ϕ_t	F	$\log\{(1-\phi_t^2)/\phi_t\}$	$-1/\phi_t + 2.3\log(1+\phi_t/1-\phi_t)$	$\log(1-F)$
59	0.172	0.00118	0.7522	-5.673	$\bar{1}$.999487
$59\frac{1}{2}$	0.339	0.00150	0.4176	-2.648	$\bar{1}$.998348
60	0.438	0.00199	0.2660	-1.875	$\bar{1}$.999131
$60\frac{1}{2}$	0.606	0.00263	0.0187	-1.038	$\bar{1}$.998857
$60\frac{3}{4}$	0.70	0.00303	-0.1375	-0.676	$\bar{1}$.998683
61	0.853	0.00346	-0.4945	-0.071	$\bar{1}$.998494
$61\frac{1}{2}$	0.938	0.00465	-0.8925	0.429	$\bar{1}$.997976

Experimental Results and Calculations for the Polymerisation of Methyl Methacrylate in the Presence of $CuBr_2$ Initiated by AIBN.

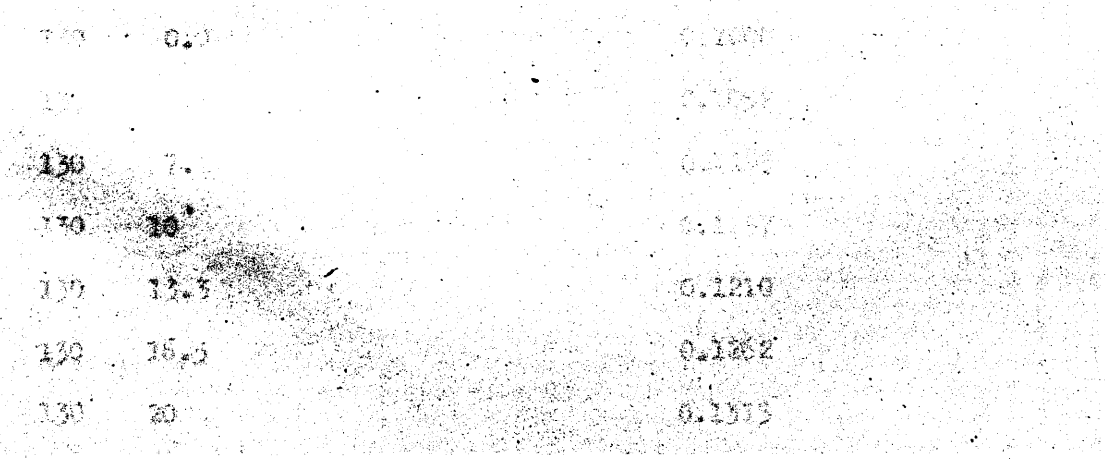
$[CuBr_2]_o = 3 \times 10^{-4}$ mole $l.^{-1}$ $[AIBN] = 5 \times 10^{-3}$ mole $l.^{-1}$

Time Measurements from recorder chart for constant drop in meniscus level.		% Polymerisation ($F \times 10^2$)
min.	sec.	
64	0.0	0.0081
64	49.5	0.0133
65	17.8	0.0184
65	46.5	0.0235
66	13.5	0.0286
66	39.3	0.0338
67	7.0	0.0389
67	25	0.0440
67	40.8	0.0492
67	58.1	0.0543
68	10.5	0.0594
68	21.3	0.0646
68	33.3	0.0697
68	41.5	0.0748
68	48.8	0.0799
68	55.8	0.0851
69	1.4	0.0902
69	5.8	0.0953
69	12.0	0.1005
69	14.8	0.1056
69	18	0.1107
69	21.5	0.1159
69	24.5	0.1210
69	28	0.1261

Time Measurements from recorder chart for constant drop in meniscus level.		% Polymerisation ($F \times 10^2$)
min.	sec.	
69	30	0.1312
69	32.8	0.1364
69	35.8	0.1415
69	38.1	0.1466
69	40.1	0.1518
69	42.8	0.1569
69	45	0.1620
69	47.8	0.1672
69	50	0.1723
69	52.1	0.1774
69.	54.3	0.1825
69	56.4	0.1877
69	58.9	0.1928
70	0.9	0.1979
70	2.9	0.2031
70	4.9	0.2082
70	6.9	0.2133
70	8.5	0.2185
70	10.3	0.2236
70	12.6	0.2287
70	14.8	0.2338
70	17.0	0.2390
70	18.9	0.2441
70	20.6	0.2492
70	22.0	0.2544
70	23.8	0.2595
70	25.6	0.2646

Reduced rates measured from conversion/time plot and calculated functions.

Time min.	Time sec.	ϕ_t	F	$\log\{(1-\phi_t^2)/\phi_t\}$	$-1/\phi_t+2.3\log(1+\phi_t/1-\phi_t)$	$\log(1-F)$
68	55	0.267	0.00084	0.5406	-3.191	$\bar{1}$.999634
69		0.328	0.00089	0.4347	-2.367	$\bar{1}$.999614
69	5	0.370	0.00094	0.3680	-1.927	$\bar{1}$.999592
69	10	0.429	0.00100	0.2800	-1.418	$\bar{1}$.999567
69	15	0.481	0.00106	0.2036	-1.029	$\bar{1}$.999538
69	20	0.529	0.00114	0.1340	-0.711	$\bar{1}$.999506
69	25	0.586	0.00122	0.0494	-0.364	$\bar{1}$.999471
69	30	0.634	0.00131	$\bar{1}$.9747	-0.079	$\bar{1}$.999432
69	35	0.683	0.00140	$\bar{1}$.8927	0.206	$\bar{1}$.999392
69	40	0.735	0.00151	$\bar{1}$.7959	0.521	$\bar{1}$.999345
69	50	0.775	0.00172	$\bar{1}$.7116	0.777	$\bar{1}$.999253



$[CuBr_2] = 4 \times 10^{-4}$ mole $l.^{-1}$ $[AIBN] = 3{\cdot}5 \times 10^{-3}$ mole $l.^{-1}$

Time measurements from recorder chart for constant drop in meniscus level.		% Polymerisation ($F \times 10^2$)
min.	sec.	
128	0.0	0.0265
128	32.1	0.0317
128	47.5	0.0370
128	59	0.0422
129	8.3	0.0475
129	14.5	0.0527
129	19.5	0.0632
129	27.5	0.0632
129	34.1	0.0685
129	39.3	0.0737
129	44	0.0790
129	49	0.0842
129	52.5	0.0895
129	56.1	0.09478
130	0.0	0.1000
130	3.1	0.1052
130	7.1	0.1105
130	10	0.1157
130	13.3	0.1210
130	16.5	0.1262
130	20	0.1315
130	23.1	0.1367
130	25.9	0.1420
130	28.1	0.1472
130	30.9	0.1525

Time measurements from recorder chart for constant drop in meniscus level.		% Polymerisation ($F \times 10^2$)
min	sec.	
130	33.3	0.1577
130	35.9	0.1630
130	38.6	0.1682
130	40.9	0.1735
130	43	0.1787
130	45.8	0.1840
130	48.5	0.1892
130	51.1	0.1945
130	53	0.1997
130	54.6	0.2050
130	57.3	0.2102
130	59.9	0.2155
131	1.6	0.2207
131	4.4	0.2260
131	6.3	0.2312
131	8.0	0.2365
131	10.3	0.2417
131	12.5	0.2470
131	14.6	0.2522
131	16.8	0.2575
131	19.3	0.2627
131	21.3	0.2680
131	24.1	0.2732
131	26.3	0.2785
131	28.1	0.2837
131	30.3	0.2890

Reduced rates measured from conversion/time plot and calculated functions.

Time		ϕ_t	F	$\log\{(1-\phi_t^2)/\phi_t\}$	$-1/\phi_t+2\cdot3\log(1+\phi_t/1-\phi_t)$	log(1-F)
min.	sec.					
129	10	0.281	0.00048	0.5149	-2.976	$\bar{1}$.999789
129	20	0.338	0.00056	0.4191	-2.262	$\bar{1}$.999757
129	30	0.398	0.00065	0.3252	-1.671	$\bar{1}$.999720
129	40	0.459	0.00075	0.2354	-1.186	$\bar{1}$.999675
129	50	0.521	0.00086	0.1456	-0.762	$\bar{1}$.999625
130	0	0.588	0.00100	0.0471	-0.353	1.999567
130	10	0.668	0.00115	$\bar{1}$.9186	0.117	$\bar{1}$.999501
130	20	0.745	0.00131	$\bar{1}$.7760	0.583	$\bar{1}$.999429